

STUDIES OF POLYMERS CONTAINING PYRENYL
AND ANALOGOUS FUNCTIONAL GROUPS

BY

DONG-WEI ZHU

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1990

UNIVERSITY OF FLORIDA LIBRARIES

*TO MY WIFE BEI-BEI, SON VANCK AND
MY FAMILY MEMBERS IN MAINLAND CHINA*

*TO THOSE WHO SACRIFICED THEIR LIVES
IN TIANANMEN SQUARE ON JUNE 4, 1989*

ACKNOWLEDGMENTS

I wish there could be something else, rather than this simple page, to express my true gratitude toward all who have been a part of my life in the last three years here at University of Florida.

First and foremost I wish to thank my research supervisor, Dr. Alan R. Katritzky, for his guidance, encouragement and pushing at the time I needed it. The decision to come to the University of Florida and to work under Dr. Katritzky's supervision is undoubtedly one of my best. What he has given to me is not only the knowledge in chemistry, but also the necessities of having a successful career life.

I would also like to thank Dr. Kirk S. Schanze for his precious help in part of my research work; Dr. James A. Deyrup for his supervising of my two year teaching in the undergraduate laboratory; Dr. James E. Garbe for his supervising of my internship at 3M Company; and other members of my graduate committee, Drs. Kenneth B. Wagener, Eric Enholm, Willis B. Person and Hendrik J. Monkhorst, for their advice and insight. My sincere appreciation is also extended to all my group and Dr. Schanze's group members, both present and past, especially to Drs. Gregory Hitchings and John Greenhill, who went through this dissertation and provided many good suggestions, and to Drs. Philip Harris,

Laslo Urogdi, Thomas Perkins and Brent MacQueen. To our office staff, Dawn Jones, Valerie Greenhill and Elizabeth Rich, I am in debt to your help and patience.

Lastly, I would like to thank all my fellow Chinese colleagues for their companionship, for the sharing of our traditions here in U.S.

TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS -----	iii
ABSTRACT -----	ix
CHAPTERS	
1 OBJECTIVES -----	1
2 SYNTHESSES AND RADICAL POLYMERIZATIONS OF MONOMERS BEARING POLYNUCLEAR AROMATIC SYSTEMS -----	3
2.1 Introduction -----	3
2.2 Results and Discussion -----	8
2.2.1 Syntheses of Monomers -----	8
2.2.2 Polymerizations and Properties of Polymers -----	16
2.3 Experimental Section -----	20
2.3.1 Apparatus and Preparations -----	20
2.3.2 Preparation of 1-Hydroxymethyl- perylene -----	22
2.3.3 Preparation of Perylen-1-ylmethyl Acrylate -----	22
2.3.4 Preparation of N-Benzylallylamine	23
2.3.5 Preparation of N-(Naphthalen-1-yl methyl)allylamine -----	24
2.3.6 Preparation of N-(Pyren-1-ylmethyl)allylamine -	25
2.3.7 Preparation of N-(Pyren-1-ylmethyl)morpholine ---	26
2.3.8 General Polymerization Procedures	26
2.4 Summary -----	27

3	INHIBITION OF 1-VINYLPERYLENE -----	28
3.1	Rationale -----	28
3.2	Results and Discussion -----	29
3.3	Experimental Section -----	35
3.3.1	Synthesis of 2,5-Dimethyl-2,5-dicyano- 3-(perylene-1-yl)hexane -----	35
3.3.2	General Procedures for Inhibition Reactions -----	36
3.4	Conclusions -----	36
4	SYNTHESES AND ADDITION POLYMERIZATIONS OF PYRENYL MONOMERS -----	37
4.1	Introduction -----	37
4.2	Results and Discussion -----	41
4.2.1	Syntheses of Monomers -----	41
4.2.2	Polymerizations -----	46
4.3	Experimental Section -----	49
4.3.1	Preparation of Diethyl Pyren-1-ylmethylidenepropanedioate	49
4.3.2	Preparation of 2-(Pyren-1-yl- methylidene)propane-1,3-diol -----	50
4.3.3	Preparation of Diethyl Pyren-1-ylmethylpropanedioate -----	51
4.3.4	Preparation of N-(Pyren-1-ylmethylidenemalononitrile	51
4.3.5	Preparation of N-(Pyren-1-ylmethyl)diethanolamine	52
4.3.6	Preparation of 2-Methyl-2-(pyren-1-yl methyl)amino-1,3-dipropanediol ---	53
4.3.7	Addition Polymerizations -----	53
4.4	Summary -----	54

5	FORMYLATION OF PENDANT AROMATIC GROUPS ATTACHED TO LINEAR POLYMER CHAINS -----	55
5.1	Introduction -----	55
5.2	Abbreviations -----	56
5.3	Results and Discussion -----	56
5.4	Experimental Section -----	64
	5.4.1 Preparation of Polymers -----	64
	5.4.2 Formylation of Polymers -----	65
	5.4.3 Reaction of Formylated Polymers with $\text{CH}_2(\text{CN})_2$ -----	65
5.5	Conclusions -----	66
6	SYNTHETIC AND PHOTOPHYSICAL INVESTIGATIONS OF SUBSTITUTED POLY(1-VINYLPYRENE) -----	67
6.1	Introduction -----	67
6.2	Results and Discussion -----	69
	6.2.1 Syntheses of Polymers -----	69
	6.2.2 Absorption Spectra -----	73
	6.2.3 Effect of Solvent and Excitation Wavelength on Substituted PVP Fluorescence -----	75
	6.2.4 Effect of Degree of Functionalization -----	82
6.3	Experimental Section -----	84
	6.3.1 General Preparations -----	84
	6.3.2 Preparation of PVP- NO_2 -----	84
	6.3.3 Preparation of PVP- NH_2 -----	85
	6.3.4 Preparation of PVP-Br -----	85
6.4	Conclusions -----	86

7	INTRAMOLECULAR CHARGE TRANSFER PROPERTIES OF ArCH=C(CN) ₂ -----	87
7.1	Introduction -----	87
7.2	Results and Discussion -----	89
7.2.1	Ground State Properties -----	89
7.2.2	Electronic Absorption Spectra ----	93
7.2.3	Fluorescence Studies -----	97
7.2.4	Solvatochromic Shifts of ICT Absorption Bands -----	103
7.2.5	The ICT Mechanism -----	107
7.3	Experimental Section -----	111
7.4	Conclusions -----	111
	BIBLIOGRAPHY -----	113
	BIOGRAPHICAL SKETCH -----	121

Abstract of Dissertation Presented to the Graduate
School of the University of Florida in Partial
Fulfillment of the Requirements of the
Degree of Doctor of Philosophy

STUDIES OF POLYMERS CONTAINING PYRENYL
AND ANALOGOUS FUNCTIONAL GROUPS

By

Dong-Wei Zhu

August, 1990

Chairman: Dr. Alan R. Katritzky
Major Department: Chemistry

Polymers containing condensed aromatic systems such as the pyrenyl group have been prepared by radical homopolymerization, copolymerization and addition polymerizations. The vinyl monomers were prepared by the Vilsmeier reaction of the aromatic compounds, followed by the Wittig reaction. Monomers to be used for addition polymerizations, which bear dihydroxy functional groups, were synthesized by using benzotriazole as a synthetic auxiliary.

1-Vinylperylene behaves as an inhibitor instead of a polymerizable monomer. Its inhibition properties were studied through the radical polymerization of styrene, methyl methacrylate, 4-vinylpyridine and vinyl acetate.

Linear poly(1-vinylpyrene) (PVP), prepared by the radical polymerization of 1-vinylpyrene, was functionalized

with -NO_2 , -CHO , -NH_2 , -Br and -CH=C(CN)_2 groups through its chemical modification in solution. The degree of substitution of the dicyanovinyl substituent was controlled from 40% to nearly 100% by variation of the reaction conditions. The other polymers were partially functionalized. The method for the formylation of linear poly(1-vinylpyrene) was extended to linear polystyrene, poly(1-vinylnaphthalene), poly(9-vinylphenanthrene) and crosslinked polystyrene.

The photophysical properties of these polymers and their corresponding monomeric compounds were studied in solution by spectroscopic methods. The influence of solvent polarity, excitation energy and degree of substitution on the emission properties of the polymers were examined.

CHAPTER 1 OBJECTIVES

The objective of this work is to prepare a series of polymers with active electro- and photophysical properties. Specifically, the project was started with the purpose of searching for materials with nonlinear optical properties [89MI, 88MI, 87MI, 84MI, 83MI].

The goal is thus to synthesize a variety of polynuclear aromatic monomers and polymerize them by free radical or condensation methods. The expected polymers would bear pendant aromatic groups such as naphthalene, pyrene, perylene and coronene. It was envisaged at the onset of the project that these polymers could possess useful electro- and photo-active properties due to the large delocalized π -electron clouds of their pendant groups. In addition, further chemical modifications, such as copolymerization of the condensed aromatic monomers with other functional monomers, were expected to afford materials with altered properties. The grafting of known chromophores to the photo-active polymeric backbones, such as poly(1-vinylpyrene) (PVP), would certainly increase the charge asymmetry and change the delocalization pattern of the π electron clouds of these polymers, and was also anticipated to enhance their performance as optical materials.

Among the polycyclic aromatics mentioned above, pyrene has been specially favored for many reasons. Besides the fact that pyrene derivatives are relatively inexpensive and easy to handle, pyrene polymers have shown active responses toward external excitations [87BCJ83, 86MA2390, 85MA1026, 85JPS(C)585]. The term 'excimer' originated from the study of concentrated pyrene solutions [60N1045, 54ZPC275].

CHAPTER 2
SYNTHESES AND RADICAL POLYMERIZATIONS OF MONOMERS
BEARING POLYNUCLEAR AROMATIC SYSTEMS

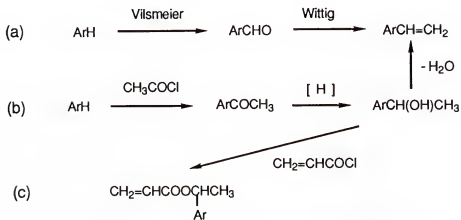
2.1 Introduction

Polymers bearing polynuclear aromatic groups are usually prepared by the polymerization of their vinyl monomers. The general procedures for the syntheses of these functional monomers are presented in Scheme 2.1.

The reaction shown in Scheme 2.1a has been the method most frequently used due to the few reaction steps and mild conditions. The requirements of reduced pressure and high reaction temperature in the dehydration step of Scheme 2.1b limits its application for the syntheses of monomers, especially when the monomers are not stable as in the cases with 1-vinylperylene and 1-vinylpyrene. The method displayed in Scheme 2.1c could be useful in cases where direct conjugation between the vinyl and polynuclear aromatic groups should be avoided, as it is with perylene. 1-Vinylperylene has been shown to be a powerful radical trap in our recent study [89MA3495, Chapter 3], whereas 1-(perylene-1-yl)ethyl acrylate, prepared as shown in Scheme 2.2, was reported to undergo free radical polymerization [72JPS(A)1345].

The syntheses of monomers with more complicated structures, such as pyrene-1-ylmethyl vinyl ketone

Scheme 2.1
Preparation of Vinylaromatics



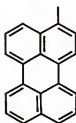
Ar :



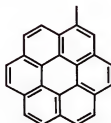
(2.1)



(2.2)

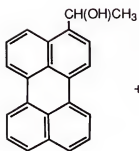


(2.3)



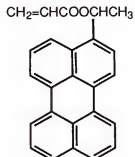
(2.4)

Scheme 2.2



(2.5)

+



(2.6)

[73BCJ358] and (4-vinylphenyl)pyren-1-ylethylene [79PP165], were completed by different methods other than those shown in Scheme 2.1.

Among the monomers in Scheme 2.1, only the polymerization of 1-vinylpyrene has been studied with different types of catalysts, as is summarized in Table 2.1.

Table 2.1
Homopolymerization of 1-Vinylpyrene

entry	type of polymn.	Mw	catalyst	ref.
1	electrochemical	13,000	SnO ₂	85MA1366
2	photochemical	9,600	n-GaAs	68JPS(L)275
3	Radical	-----	BPO	68BCJ2719
4	Ziegler-Natta	340,000	AlEt ₃ /TiCl ₄	85MA1366
5	Anionic	-----	Sodium Naphthalene	69BCJ2406
6	Anionic	637,000	Cumyl Potassium	72MA158
7	Anionic	297,000	α -MeSK	72MA158
8	Cationic	-----	BF ₃ /OEt ₂	87BCJ83

Such polymerizations generally need to be carried out under inert atmospheres, and require the use of high purity monomers. Since 1-vinylpyrene forms normal living polymeric anions and neither chain transfer to monomer nor the formation of 'dormant' polymer anions occurred when cumyl potassium was used as the catalyst, this method

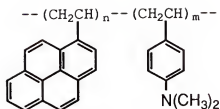
afforded the highest M_w [72MA158]. All the polymers listed in Table 2.1, including those prepared with the Ziegler-Natta catalyst, are atactic, although a high degree of crystallinity caused by the side chain-side chain interactions of the bulky pendant pyrene group has been noticed [86MA2390].

By contrast, reports of the polymerizations of other polycyclic aromatic monomers are very scarce. 1-Vinylcoronene [86MC(C)549], 1- and 9-vinyanthracenes, and 9-vinylphenanthrene [63JPS(A)1635] have been polymerized only radically, and no detailed discussion was given.

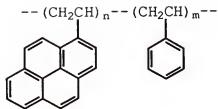
Copolymerizations have also been reported in attempts to obtain new materials as illustrated in Figure 2.1.

Polymers 2.8, 2.12 and 2.13 in Figure 2.1 were prepared by living anionic polymerizations and are therefore block copolymers. Polymer 2.13 was obtained by the polymerization of 1-vinylpyrene with trimethylsilyl methacrylate, followed by hydrolysis of the trimethylsilyl group. The rest of the polymers were synthesized by free radical polymerization procedures. Interestingly, polymers 2.9 and 2.11 are amphiphilic copolymers due to the presence of the sulfonic acid anion. Those polymers are water soluble when the ratios of the pyrene unit and phenanthrene unit relative to the sulfonic anion are less than 35% and 58%, respectively.

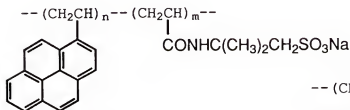
However, the published studies of such copolymerizations are preliminary in nature. Emphasis has



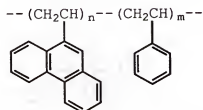
(2.7) [85JPS (C) 585]



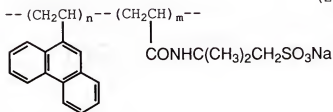
(2.8) [72MA158]



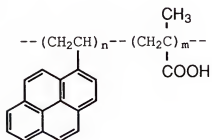
(2.9) [82JPS (C) 467]



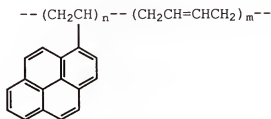
(2.10) [63JPS (A) 1635]



(2.11) [82JPS (C) 467]



(2.13) [82JPS (C) 2007]



(2.12) [72MA158]

Figure 2.1. Polymers Containing Condensed Aromatic Groups

been placed on testing the copolymer properties rather than on investigation of the polymerization processes.

The present study was therefore initiated with the purpose of performing a systematic study of the photophysical properties of the polymers with respect to their structures. It was rationalized that such an investigation could provide some insight into the photophysical behavior of the homo- and copolymers containing pendant aromatic groups.

2.2 Results and Discussion

2.2.1 Syntheses of Monomers

Table 2.2
Syntheses of Monomers

monomer	m.p. or b.p. °C		yield ^a	ref.
	found	lit.		
1-Vinylpyrene (VPy)	88-89	88-89 ^b	70	68BCJ2719
1-Vinylnaphthalene (VN)	96/4mm	133/18mm ^c	91	67JOM518
1-Vinylperylene (VPe)	143-6	153-4 ^b	62	80BPJ55
1-Vinylcoronene (VCo)	168-70	170 ^b	34	86MC(C)549

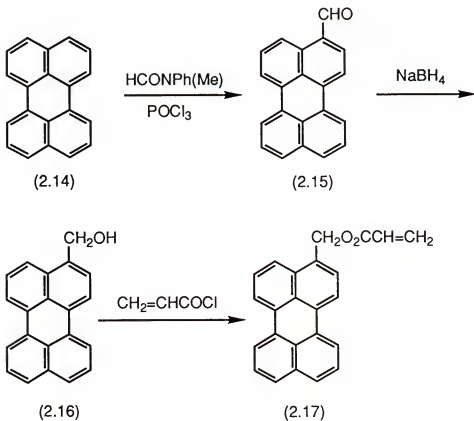
^a Yields from aldehyde except for VPe(overall yield). ^b Melting point. ^c Boiling point.

The monomers listed in Table 2.2 were synthesized by the method shown in Scheme 2.1a. All are known compounds, and literature procedures were followed in their preparations with the following modifications.

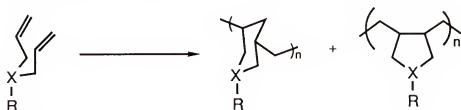
Perylene-1-carboxaldehyde (2.15), synthesized by the Vilsmeier reaction [38JA2555], is not easily purified by recrystallization or column chromatography, due to its poor solubility in most organic solvents. It was therefore used without purification in the synthesis of 1-vinylperylene and the overall yield was much improved over that previously reported (62% compared with 36.6%) [80BPJ55]. Tanikawa [68BCJ2719] described the reaction of pyrene-1-carboxaldehyde with methyl triphenylphosphonium ylide in refluxing THF for 24 h. However, we have shown that the reaction was completed within 2 h. at room temperature. Longer reaction times are undesirable due to the possible induction of polymerization of the reactive 1-vinylpyrene.

As will be discussed in detail in Chapter 3 1-vinylperylene behaves as a radical trap instead of a polymerizable monomer. Perylene-1-ylmethyl acrylate was therefore prepared by the method shown in Scheme 2.3. The color of the solution turned from dark red to green when perylene-1-carboxaldehyde was reduced. Concentrated HCl has been used to quench the reduction [70JOC2707]. However, the use of water was found to be preferable since concentrated HCl resulted in a mixture of 1-hydroxymethylperylene and 1-chloromethylperylene. The reaction of acryloyl chloride with the alcohol was catalyzed by pyridine and the yield of this monomer was about 35%. It was anticipated that this monomer, with the

Scheme 2.3
Preparation of (Perylen-1-yl)methyl Acrylate



Scheme 2.4
Cyclopolymerization of Diallyl Monomers



X: N, C, or O (No R attached)

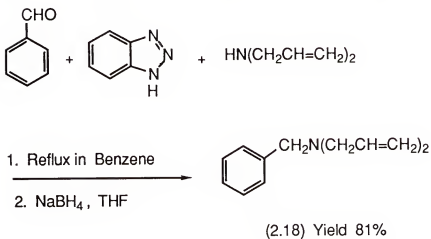
R: Aromatic or Aliphatic Groups

isolated double bond, would be much less affected by the inhibitory effect of its perylene substituent.

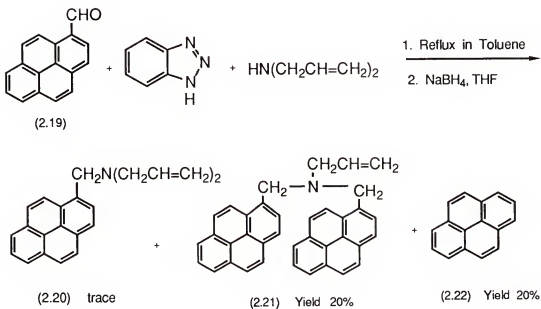
Monomers with the potential of being cyclopolymerized have also been investigated. As illustrated in Scheme 2.4, many monomers with the 1,6-diene structure have been cyclopolymerized [75JMS(C)97], since the reaction was first reported by Butler in 1951 [51JA895].

Using benzotriazole as a synthetic auxiliary in the reaction of benzaldehyde and diallylamine, resulted in the formation of the Mannich type adduct shown in Scheme 2.5. The product, N-benzylldiallylamine, was obtained in high yield by the reductive removal of benzotriazolate using NaBH_4 . N-(Pyren-1-ylmethyl)morpholine was also prepared from pyrene-1-carboxaldehyde, benzotriazole and morpholine in a 50% yield by the same method. However, the desired N-(pyren-1-ylmethyl)-diallylamine (2.20) was obtained only in a trace amount by the method shown in Scheme 2.6, and the separated products were N,N'-bis(pyren-1-ylmethyl)-allylamine (2.21) and pyrene. The latter reaction did not go to completion even when the generated water was continuously removed with the aid of a Dean-Stark trap. The theoretical amount of water could not be collected and the presence of an aldehyde residue was clearly indicated by the NMR analysis of the crude product even after overnight reflux in benzene. However, when benzaldehyde was used as the substrate, the aldehyde peak disappeared within 2 h. under similar reaction conditions. No improvement was observed by varying the reaction

Scheme 2.5
Preparation of N-Benzylldiallylamine



Scheme 2.6

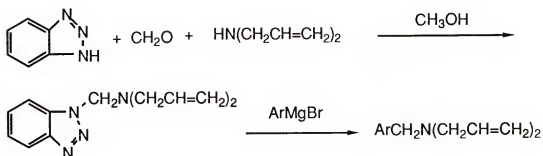


conditions; for instance, refluxing in toluene instead of benzene, stirring overnight at room temperature in the presence of a drying agent, or reducing the molar ratio of the pyrene-1-carboxaldehyde to half of its theoretical amount. Both compound 2.21 and pyrene were formed in the reduction step as was indicated by NMR of the intermediate adduct. The mechanism of the formation of compound 2.21 was not clear. However, the recovery of pyrene was not unusual since pyrene was found as a by-product in many of the subsequent reactions, especially reductions at elevated temperatures.

Naphth-1-aldehyde also failed to give the expected product under similar reaction conditions.

Alternatively, compounds 2.20 and 2.24 were successfully synthesized by the reaction of Grignard reagents with the benzotriazole intermediate 2.23 as shown in Scheme 2.7. Adduct 2.23 was obtained simply by stirring formaldehyde, benzotriazole and diallylamine in methanol for an hour followed by evaporation of solvent. Its ^1H and ^{13}C NMR spectra were complicated by the equilibrium shown in Scheme 2.8. It has been reported that N-aminoalkylbenzotriazoles generally exist as mixtures of two isomers, i.e., the 1-benzotriazolyl (structure 2.23) and the 2-benzotriazolyl 2.26 [87JCS(P1)2673]. The equilibrium lies to the left due to the greater resonance stabilization of adduct 2.23 as demonstrated in Scheme 2.8.

Scheme 2.7
Preparation of N-Substituted Diallylamino Monomers

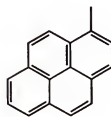


(2.23)

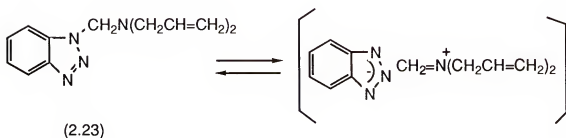
Ar:



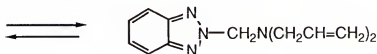
(2.24) Yield: 82%



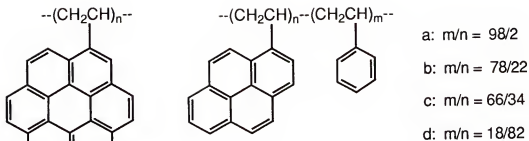
(2.20) Yield: 84%

Scheme 2.8

(2.23)



(2.25)



(2.8)

(2.26)

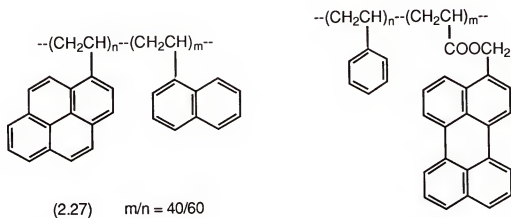
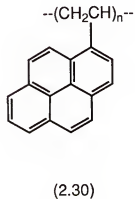
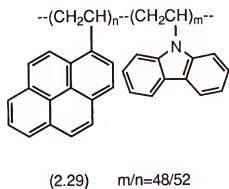
(2.28) $m/n = 6/94$ 

Figure 2.2. Structures of polymers prepared by Free Radical Homo- And Copolymerizations

2.2.2 Polymerizations and Properties of Polymers

The polymers in Figure 2.2 were prepared by free radical polymerizations using azobis(2-methylpropionitrile) (AIBN) as the initiator. In most cases, monomer residues in the resulting polymers were removed by refluxing with methanol in a Soxhlet.

The polymers are colorless or yellow powders and exhibit strong fluorescence under UV light. They are soluble in THF, DMSO, DMF, benzene and dichloromethane, but not in hexane or alcohols.

Polymers with varying concentrations of pyrene units (2.8) were prepared with the purpose of investigating the intramolecular interactions of the pyrene units as a function of the separation distance. Copolymerization of 1-vinylpyrene with styrene in different feeding ratios afforded a series of 2.8 copolymers. Statistically, the higher the percentage of pyrene, the closer the distances between the two adjacent pyrene units in the polymeric chain.

It can be seen from Table 2.3 that the percentages of pyrene units are higher in the resulting polymers than in their feedstock mixtures. Since the copolymer composition is closely related to the reactivity of the monomers, it can be assumed that 1-vinylpyrene is more reactive than styrene or 1-vinylnaphthalene to free radical polymerizations, in spite of the fact that it has the more bulky pendant group. The reactivity ratio of 1-vinylpyrene with other monomers was not studied. However, its

Table 2.3
Polymerization and Copolymerization of 1-Vinylpyrene

polymer	feeding molar ratio	unit ratio in copolymer ^a	conversion ^b	Mw	Mw/Mn
<u>2.7a</u>	St:VPy = 99:1	98:2	>97	47,000	1.83
<u>2.7b</u>	St:VPy = 90:10	78:22	97	27,700	2.30
<u>2.7c</u>	St:VPy = 87:13	66:34	93	16,500	1.99
<u>2.7d</u>	St:VPy = 50:50	18:82	73	30,900	2.12
<u>2.27</u>	VN:VPy = 66:34	40:60	52	21,900	2.15
<u>2.28c</u>	St:PeMA = 97:3	94:6	62	13,000	1.79
<u>2.29</u>	VC:VPy = 50:50	48:52	56	8,000	2.90
<u>2.26d</u>	VCO	homopolymer	34	-----	-----
<u>2.30</u>	VPy	homopolymer	64	32,200	2.15

^a Unit ratios in copolymers were calculated from the UV absorption peak in 331 nm with poly(1-vinylpyrene) as standard and THF as solvent.

^b Conversions based on 1-vinylpyrene. ^c Calculated from UV at 441 nm; conversion based on perylen-1-ylmethyl acrylate. ^d Conversion based on Coronene.

reactivity should be close to that of 9-vinylcarbazole (VC) since their compositions hardly changed during copolymerization.

The composition of VC-VPy copolymer 2.29 was determined by both elemental analysis and its UV absorption spectrum. The deviation between the two methods is within 2%. The unit ratio of all the other polymers in Table 2.3 was obtained from their UV spectra with pyrene, perylene or coronene as references, respectively.

In contrast with a literature report [72JPS(A)1345], perylen-1-ylmethyl acrylate (2.17) could not be homopolymerized radically, though it can be copolymerized with styrene in a low percentage. The highest molar percentage of monomer 2.17 that could be incorporated into polymer 2.28 was only 6%.

The results of the cyclopolymerization of the diallylamino monomers 2.20 and 2.24 were not satisfactory. Monomers were partially recovered when they were polymerized according to the reported method [76JMS(C)923]. The residues usually gave very complicated results on NMR and GC-MS analysis with monomer and pyrene being present as major components. Polymerization in acidic aqueous solution with ammonium persulfate also failed to yield the expected polymer.

The UV-visible absorption spectra of polymers 2.8, 2.27, 2.29 and 2.30 are similar to that of pyrene in THF solution, except that the bands above 300 nm are red-shifted about 10 nm and broadened. However, the relative

Table 2.4
UV Spectra of Polymers Containing Pyrene Units

compounds	relative absorption intensity (λ_{\max} nm)			
Pyrene	1.00(336)	0.62(321)	1.00(274)	0.53(263)
P(VPy) (2.27)	1.00(348)	1.00(331)	-----	0.69(268)
P(VPy-St) (2.7a)	1.00(346)	0.69(330)	0.29(278)	0.75(265)
P(VPy-St) (2.7b)	1.00(346)	0.78(330)	0.14(278)	0.64(266)
P(VPy-St) (2.7c)	1.00(346)	0.80(330)	0.61(278)	0.85(266)
P(VPy-St) (2.7d)	1.00(348)	0.96(330)	-----	0.67(267)
P(VPy-VN) (2.28)	1.00(346)	0.89(330)	-----	0.81(266)
P(VPy-VC) (2.29)	1.00(346)	1.05(330)	1.45(278)	1.40(265)

absorption coefficients at different λ_{\max} were not the same. The values in Table 2.4 were obtained by ξ_x/ξ_1 , where ξ_1 is the absorption coefficients of bands at the longest wavelength (Column 1).

It can be seen that polymers with pyrene pendant groups have stronger absorptions at longer wavelengths than pyrene does. The absorption band around 330 nm is in proportion to the number of pyrene units in the polymer. In the homopolymer of 1-vinylpyrene, it becomes as strong as that at 348 nm.

It is interesting that in the copolymer of VPy and VC (2.29), the relative absorption intensities are in reverse order to that of all the other polymers. Since the two monomer units are in nearly a 1:1 unit ratio in the copolymer, this exceptional behavior in UV spectra may

result from the ground state interaction between pyrene and carbazole. Poly(9-vinylcarbazole) is known to be a good semi-conducting material and is the only one prepared on a industrial scale [86MI489].

The UV spectra of polymers 2.26 and 2.28 are exactly the same as those of coronene and perylene, respectively.

2.3 Experimental Section

2.3.1 Apparatus and Preparations

Melting points were determined on a Kofler hot-stage microscope and are not corrected. Spectra were recorded with the following instruments: ^1H -NMR spectra with a Varian Model VXR 300 spectrometer running at 300 MHz using Me_4Si as an internal reference; ^{13}C -NMR with the same machine running at 75 MHz, referencing to the center signal of CDCl_3 (77.0 ppm) or $[\text{}^2\text{H}_6]\text{-DMSO}$ (39.5 ppm). Mass spectra were obtained at 70 eV on an AEI MS 30 spectrometer operating with a DS-55 data system. Elemental analysis was performed under the supervision of Dr. R. W. King and Dr. D. Powell of the Department of Chemistry. Gel Permeation Chromatography spectra (GPC) were obtained by a Water Associates Model M 6000A HPLC with Model U6K injector and Perkin-Elmer LC-75 Spectrophotometric Detector using THF as solvent. The GPC data of THF insoluble samples were obtained from the 3M Center. All the molecular weights are based on standard polystyrene samples, and not corrected. The UV detector was set at 340 nm for pyrene polymers since

they have two strong absorption bands in the 330 to 350 nm region. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR, and UV on a Perkin-Elmer 330 Spectrophotometer. Steady-state luminescence spectra were measured on a Spex Industries F-112A spectrophotometer. Emission spectra were corrected for instrument response using correction factors generated by using a tungsten filament primary standard lamp. Excitation spectra were corrected by using a Rhodamine B/1,2-propanediol quantum counter reference. Solvents used in the photophysical studies, except B&J spectrophotometric grade brand, were purified by routine procedures and checked under the measurement conditions prior to use. Solution concentrations were adjusted so that the absorbance at the excitation wavelengths was less than 0.1 for all the emission and excitation measurements.

All moisture sensitive reactions were carried out in oven-dried apparatus (120°C overnight) under a slight positive pressure of dry nitrogen and transfer operations were carried out by syringe techniques.

Diethyl ether and tetrahydrofuran (THF) were freshly distilled from sodium-benzophenone. Benzene and toluene were distilled over metallic sodium and stored over 4 Å molecular sieves. AIBN was recrystallized from 95% ethanol and stored in a refrigerator.

The above instruments and general preparative methods were used for all the work described in this dissertation.

1-Vinylpyrene, 1-vinylnaphthalene, 1-vinylperylene and 1-vinylcoronene were synthesized by reported methods. Their yields, melting or boiling points and references are listed in Table 2.2.

2.3.2 Preparation of 1-Hydroxymethylperylene (2.16)

Crude perylene-1-carboxaldehyde (5.0 g, 21.7 mmol) was added to a stirred solution of NaBH_4 (1.0 g, 26.5 mmol) in THF (250 ml) and the mixture refluxed for 10 h. Water was added (5 ml) and the solvents were evaporated at reduced pressure. The residue was extracted with refluxing benzene (2x250 ml). The combined benzene solutions, upon standing overnight, afforded bright yellow needle crystals of 1-hydroxymethylperylene (2.88 g, 57%, mp. 209–211°C. Lit. 175°C dec. [70JOC2707]). NMR: ^1H (δ ppm/TMS): 7.45–8.28, m, 11H (aromatic); 5.35, t, 1H (OH); 4.93, d, 2H (CH_2). ^{13}C (δ ppm/DMSO): 137.6; 134.2; 131.8; 130.7; 130.5; 130.4; 129.5; 128.0; 127.7; 127.4; 126.6; 126.5; 125.1; 123.6; 120.4; 120.3; 120.1; 120.0 (aromatics); 61.3 (CH_2). Analysis: for $\text{C}_{21}\text{H}_{14}\text{O}$ calculated: C:89.34, H:5.00; found: C:89.12, H:4.95.

2.3.3 Preparation of Perylen-1-ylmethyl Acrylate (2.17)

To a solution of 1-hydroxymethylperylene (2.0 g, 7.1 mmol) in THF (130 ml) under dry nitrogen, thionyl chloride (1.0 ml, 13.7 mmol) was injected, followed by pyridine (0.6 ml, 7.8 mmol). The mixture was kept at 50°C for 2.5 h. and the precipitate was removed by filtration. The residue,

obtained by the removal of solvent at reduced pressure, was dissolved in CH_2Cl_2 and washed with aqueous HCl and water. The CH_2Cl_2 layer was then dried with molecular sieves. Removal of solvent afforded the crude product. It was purified by several recrystallization from benzene (0.90 g, 38%, mp. 173–175°C). NMR: ^1H ($\delta\text{ppm/TMS}$): 7.43–8.21, m, 11H (aromatic); 6.47, q, 1H; 6.19, q, 1H; 5.86 q, 1H ($\text{CH}_2=\text{CH}$); 5.57, s, 2H (CH_2). ^{13}C ($\delta\text{ppm/DMSO}$): 166.0 (CO); 134.2; 132.9; 137.8; 131.3; 131.0; 130.8; 130.7; 128.9; 128.4; 128.3; 128.2; 128.1; 128.0; 127.0; 126.6; 126.5; 123.3; 120.5; 120.4; 120.3; 119.5 (aromatic and vinyl); 64.7 (CH_2). Analysis: for $\text{C}_{24}\text{H}_{16}\text{O}_2$ calculated: C:85.69, H:4.79; found: C:85.94, H:4.75.

2.3.4 Preparation of N-Benzylallylamine (2.18)

Benzotriazole (4.0 g, 33.4 mmol), diallylamine (3.0 g, 31.0 mmol) and benzaldehyde (3.16 g, 31.1 mmol) were dissolved in benzene (100 ml) and refluxed under a Dean-Stark trap for 2 h. Separation of water was noticed. After removal of the solvent, the residue was added to an equimolar amount of NaBH_4 in THF (60 ml) and stirred overnight to ensure the complete reductive removal of the benzotriazole. The excess NaBH_4 was then decomposed by dilute HCl, the THF evaporated and the residue extracted with ether. The ether layer was washed with aqueous NaOH and H_2O , and the solvent was evaporated to afford (2.18) as a colorless liquid (4.6 g, 82%). NMR: ^1H ($\delta\text{ppm/TMS}$): 7.36–7.32, m, 5H (aromatic); 5.89, m, 2H ($\text{CH}=\text{CH}$); 5.27, q,

4H(CH₂=); 3.57, s, 2H(CH₂); 3.08, d, 4H (CH₂).
¹³C(δppm/CDCl₃): 139.4; 135.8; 128.1; 128.9; 126.8; 117.3
 (aromatic and vinyl); 57.5 (CH₂); 56.4 (CH₂). Analysis:
 calculated for C₁₃H₁₇N: C:83.37, H:9.15, N:7.48; found:
 C:83.38, H:9.15, N:7.43.

2.3.5 Preparation of N-(Naphthalen-1-ylmethyl)diallylamine (2.24)

Benzotriazole (2.9 g, 24.3 mmol), diallylamine (2.13 g, 22.0 mmol) and formaldehyde (1.81 g, 36.5% aqueous solution, 22.0 mmol) were mixed and dissolved in methanol (10 ml). After overnight stirring the solvent was removed at reduced pressure, and the residue dried in benzene solution (10 ml) with MgSO₄. This solution was added to a Grignard reagent, made from 1-bromonaphthalene (4.76 g, 23.0 mmol) and Mg (0.85 g, 35.0 mmol) in ether (20 ml), and the mixture stirred at room temperature overnight, before being quenched with 25% aqueous NH₄Cl (25 ml). The aqueous layer was separated and extracted with ether (20 ml). The combined ether layers were washed with 5% NaOH, water and dried. Pure product was obtained by removal of solvent at reduced pressure followed by column chromatography (silica gel, eluted with 1:1 hexane:dichloromethane) (3.12 g, 60%).
 NMR: ¹H(δppm/TMS): 8.28, d, 1H; 7.78, m, 2H; 7.45, m, 4H (aromatic); 5.93, m, 2H (CH=); 5.28, q, 4H (CH₂=); 3.98, s, 2H (CH₂); 3.14, d, 4H (CH₂). ¹³C(δppm/CDCl₃): 164.7; 135.7; 133.8; 132.4; 128.4; 127.7; 127.2; 125.6; 125.5; 125.1; 124.6; 117.6 (aromatic and vinyl); 56.8 (CH₂); 56.0

(CH₂). Analysis: calculated for C₁₇H₁₉N: C:86.03, H:8.07; found: C:85.90, H:8.80.

2.3.6 Preparation of N-(Pyren-1-ylmethyl)diallylamine (2.20)

1-Bromopyrene (17.3 g, 61.6 mmol) dissolved in dry THF (150 ml) was added dropwise to Mg (2.0 g, 83.3 mmol) suspended in THF (10 ml) over a period of 5 h. whilst refluxing under dry nitrogen. A dark-brown solution of the corresponding Grignard reagent resulted. BtCH₂N(CH₂CH=CH₂)₂ (prepared as in 2.3.5 from benzotriazole, 9.5 g, 41.7 mmol) in THF (25 ml) was added slowly to this solution with vigorous stirring. The mixture became white at the end of the addition with the formation of a precipitate. The reaction was kept at ambient temperature overnight and quenched with saturated NH₄Cl (40 ml). The organic layer was separated and the solvent evaporated at reduced pressure. The residue was then purified by column chromatography (silica gel, hexane:dichloromethane = 1:1). The product (7.6 g, 58%, mp. 65–66°C) was eluted after pyrene (3.6 g). NMR: ¹H(δppm/TMS): 8.41, d, 1H; 7.84–8.02, m, 8H (aromatic); 5.89, m, 2H (CH=); 5.15, m, 4H (CH₂=); 4.08, s, 2H (CH₂); 3.08, d, 4H (CH₂). ¹³C(δppm/CDCl₃): 135.7; 133.0; 131.2; 130.8; 130.5; 129.7; 127.9; 127.3; 126.9; 126.8; 125.6; 124.9; 124.8; 124.7; 124.6; 124.3; 124.0; 117.6 (aromatic and vinyl); 56.8 (CH₂); 56.0 (CH₂). Analysis: calculated for C₂₃H₂₁N: C:88.71, H:6.80, N:4.50; found: C:88.34, H:6.77, N:4.28.

2.3.7 Preparation of N-Pyren-1-ylmethylmorpholine

Pyrene-1-carboxaldehyde (3.5 g, 15.2 mmol), benzotriazole (2.0 g, 16.8 mmol) and morpholine (1.48 g, 17.0 mmol) were dissolved in benzene (100 ml) and refluxed for 5 h. under a Dean-Stark trap. The product after the removal of benzene at reduced pressure, was added to an equimolar amount of NaBH_4 in THF (50 ml) and kept at room temperature for 2 days. Water (5 ml) was added and the solvents evaporated. The residue was dissolved in ether and washed with 5% aqueous NaOH and H_2O . Removal of the ether afforded an oily residue, which was triturated with hexane (30 ml) to give the prism crystals above (2.2 g, 49%, mp. 90-92°C). NMR: ^1H (δ ppm/TMS): 7.94-8.47, m, 9H (aromatic); 4.09, s, 2H (CH_2); 3.58, t, 4H (CH_2); 2.48, t, 4H (CH_2). ^{13}C (δ ppm/ CDCl_3): 129.7; 129.1; 128.7; 128.6; 127.7; 126.5; 125.5; 125.2; 124.2; 123.2; 122.6; 122.4; 122.3 (aromatic); 64.7 (CH_2); 59.3 (CH_2); 51.7 (CH_2). Analysis: calculated for $\text{C}_{21}\text{H}_{19}\text{NO}$: C:83.69, H:6.35, N:4.65; found: C:83.62, H:6.37, N:4.56.

2.3.8 General Polymerization Procedures

All the polymers described in this chapter were obtained by the free radical polymerization method described below: The monomer was dissolved in dry benzene or toluene to a concentration of 10% by weight with AIBN as initiator (1% of monomer). The reaction flask was purged with nitrogen and stirred at 60°C overnight to complete the polymerization. The resulting solution was poured into

four times of its volume of methanol to give the polymer which was purified by refluxing with ethanol in a Soxhlet to remove monomer residues.

2.4 Summary

Homo- and copolymers containing condensed aromatic systems such as pyrene, perylene and coronene have been prepared by radical polymerizations. The vinylaromatic monomers were prepared by Vilsmeier's reactions followed by Wittig's reactions. Monomers with potential for cyclopolymerization have also been synthesized by using benzotriazole as an auxiliary. The copolymer of styrene and 1-vinylpyrene was obtained in a series of unit ratios with the intention of investigating the intramolecular interaction of the pyrene chromophore as a function of separation distance. A preliminary photophysical study disclosed that there is not a strong interaction between the chromophores present in the ground state of the prepared copolymers except that from 1-vinylpyrene and 9-vinylcarbazole.

CHAPTER 3 INHIBITION OF 1-VINYLPERYLENE

3.1 Rationale

1-Vinylperylene (VPe, 2.3) has been previously prepared [80BPJ55] as shown in Chapter 2, but there is no report of its polymerization or attempted polymerization in the literature. Polymers bearing pendant perylene groups have been prepared from monomers in which the vinyl groups were not directly conjugated with perylene [72JPS(A)1345].

It was found during the present work, however, that 1-vinylperylene could not be polymerized and further that it strongly inhibits the radical polymerization of reactive monomers.

Steric hindrance by the large perylene aromatic ring system could not be the explanation for this in view of the facile radical polymerization of 1-vinylpyrene (2.2). 1-Vinylpyrene is actually more reactive than styrene when they are copolymerized [Chapter 2].

It is true that not all organic compounds possessing carbon-carbon double bonds undergo radical polymerization. For instance, trans-stilbene resists to be polymerized in the presence of any radical initiator. Nevertheless, trans-stilbene does not behave as an inhibitor. Radical polymerization of styrene proceeded readily with AIBN (1.0

wt.% of monomer) in the presence of trans-stilbene in the same concentration as AIBN.

In an attempt to further investigate the properties of polycyclic aromatics, the behavior of 1-vinylperylene in the presence of an initiator and reactive monomers was examined and compared with that of perylene.

3.2 Results and Discussion

After attempts to polymerize or copolymerize 1-vinylperylene under normal free radical conditions failed, we investigated the effects of small quantities of added VPe on the AIBN initiated polymerizations of styrene, methyl methacrylate, 4-vinylpyridine and vinyl acetate. The results are shown in Figure 3.1. The polymerization of vinyl acetate is completely inhibited when the VPe molar concentration equals that of the initiator. For the other three monomers, the polymerization is strongly retarded by a concentration of VPe double that of the initiator and completely stopped by three times the concentration.

Results suggest that VPe reacts with the initiator radicals as shown in Scheme 3.1. The reactive vinyl group of VPe traps $\text{Me}_2\dot{\text{C}}\text{CN}$ radicals, either immediately on their release from AIBN or, in the early growth of the polymer chain, with the formation of radical 3.1. Radical 3.1 is insufficiently reactive to initiate polymerization and, therefore couples with another $\text{Me}_2\dot{\text{C}}\text{CN}$ or undergoes dimerization. On the other hand, the freshly released

$\text{Me}_2\dot{\text{C}}\text{CN}$ reacts faster with radical 3.1 (to give compound 3.2) than with the unreactive vinyl acetate monomer, but slower than with reactive monomers, such as styrene. Hence, an equal molar ratio amount of VPe to AIBN suffices to inhibit the vinyl acetate while a double molar ratio is needed for the inhibition of the other three monomers.

From the kinetic point of view, $K_2[\text{M}]$ is smaller than, or close to $K_{2i}[\text{I}]$ in Eq.3 of Scheme 3.2 when the amount of added 1-vinylperylene equals that of the initiator in the polymerization of vinyl acetate. While for the other monomers the amount of 1-vinylperylene must equal twice that of the initiator for this to be true.

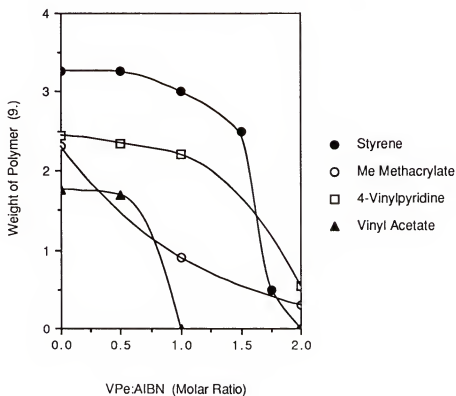
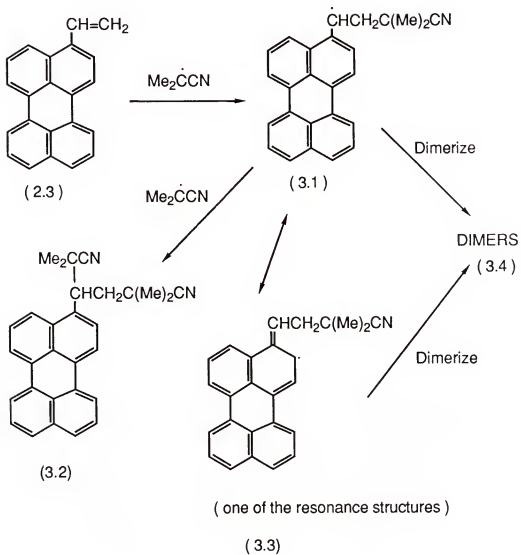


Figure 3.1. Inhibition effect of 1-vinylperylene (VPe) on the polymerizations.

Scheme 3.1
Reaction of 1-Vinylperylene With AIBN



Scheme 3.2
Kinetics of Inhibition [64M645]

propagating free radical + monomer ----> growing chain

$$-\frac{d[M]}{dt} = K_2[RM\cdot][M] \quad \text{Eq. 1}$$

propagating free radical + inhibitor ---->
unreactive product

$$-\frac{d[RM\cdot]}{dt} = -\frac{d[I]}{dt} = K_{2i}[RM\cdot][I] \quad \text{Eq. 2}$$

molecular weight of the resulting polymer

$$\bar{M}_n = \frac{K_2[M]}{K_{2i}[I]} \quad \text{Eq. 3}$$

The reaction of 1-vinylperylene with a large quantity of AIBN supported this interpretation. 2,5-Dimethyl-2,5-dicyano-3-(perylene-1-yl)hexane (3.2) (16%) was obtained as orange crystals when 1-vinylperylene was refluxed with 3 moles of AIBN in benzene for 24 hr. However, if the molar ratio of AIBN to 1-vinylperylene was 1:1, a yellow precipitate formed as the main product under the same reaction conditions. It had a melting point >340°C and could not be dissolved in solvents such as THF, cyclohexane, DMSO, trifluoroacetic acid, toluene or chloroform. The IR spectrum showed the strong characteristic perylene bands at 809 and 761 cm⁻¹, but not the vinyl peaks at 985 and 905 cm⁻¹ [80BPJ55]. Furthermore, since its elemental analysis is very close to that of the radical 3.1, the yellow precipitate was deduced

to be the dimer 3.4 (see Scheme 3.1). Presumably, it is a mixture of several isomers.

It has been reported that perylene can inhibit the polymerization of vinyl acetate with an experimental stoichiometric coefficient of 2.03 [66EPJ219]. The authors calculated that perylene has the largest delocalization energy of a series of polynuclear aromatic compounds. Nevertheless, neither the exact mechanism of inhibition, nor the properties of the inhibitor were mentioned.

Figure 3.2 indicates that vinyl acetate is the only monomer investigated that perylene can inhibit. In fact, our experimental results disclosed that perylene is rather inert to most of the radicals. Perylene is recovered when it is refluxed in benzene/cyclohexane (5:3 by volume) with an equivalent amount of AIBN for 24 h.

As can be seen from Scheme 3.3, vinyl acetate is the least reactive monomer of those studied. Its poorly stabilized radical could be reactive enough to attack perylene to give an unreactive species. The polymerization was thus inhibited. For the same reason, the polymerization of vinyl acetate is very sensitive to many different types of impurities present in low concentrations [50JA1051]. For the other monomers, their vinyl groups are more reactive due to conjugation. The resulting radicals are thus less reactive and more selective. These monomers therefore react at the growing radical center to form the polymers.

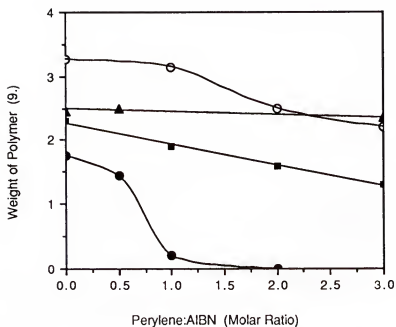
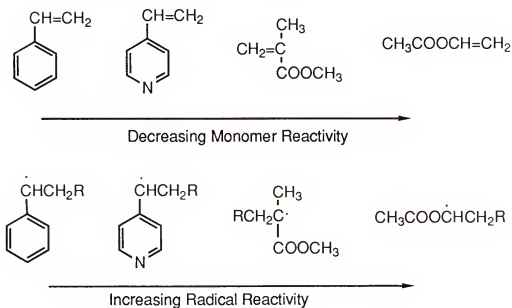


Figure 3.2. Inhibition effect of perylene on the polymerizations. (○) Styrene, (▲) Methyl Methacrylate, (■) 4-Vinylpyridine, (●) Vinyl Acetate.

Scheme 3.3
Reactivity of Monomer vs Radical



3.3 Experimental Section

AIBN was recrystallized from 95% ethanol. Styrene was washed with aqueous 5% NaOH to remove the inhibitor. It was then washed with water, dried with MgSO_4 and distilled under nitrogen at reduced pressure. 4-Vinylpyridine was distilled before use. Vinyl acetate was refluxed with a small amount of benzoyl peroxide and distilled under nitrogen. Methyl methacrylate was washed with 5% aqueous NaOH, water, then dried with MgSO_4 and distilled under nitrogen at reduced pressure.

1-Vinylperylene was prepared by the reported method [80BPJ55] as discussed in Chapter 2.

3.3.1 Synthesis of 2,5-Dimethyl-2,5-dicyano-3-(perylene-1-yl)hexane (3.2)

1-Vinylperylene (0.50 g, 1.8 mmol) was refluxed with AIBN (0.89 g, 5.4 mmol) in benzene/cyclohexane (5:3 by volume, 20 ml) under nitrogen for 24 h. After the removal of the solvents, the product was obtained by column chromatography (silica gel, CH_2Cl_2 :benzene = 1:1) and further purified by recrystallization from ethyl acetate (0.12 g, 16%, mp. 240-242°C). NMR: ^1H (δ ppm/TMS): 7.26-8.26, m, 11H (aromatic); 2.44, m, 1H (CH); 1.64, s, 3H (CH₃); 1.56, d, 2H (CH₂); 1.39, s, 3H (CH₃); 1.10, s, 3H (CH₃); 0.90, s, 3H (CH₃). ^{13}C (δ ppm/ CDCl_3): 135.6; 134.1; 133.7; 131.9; 130.6; 130.3; 128.8; 128.0; 127.7; 127.0; 126.3; 124.8; 124.0; 123.8; 122.0; 120.3; 120.2; 120.1;

120.0; 119.5 (aromatic); 43.4 (C); 43.0 (C); 37.9 (CH); 32.9 (CH₂); 28.0 (CH₃); 26.9 (CH₃); 25.8 (CH₃); 24.4 (CH₃). Analysis: calculated for C₃₀H₂₆N₂: C:86.92, H:6.32, N:6.76; found: C:86.58, H:6.28, N:6.25.

3.3.2 General Procedures for Inhibition Reactions

All the inhibition reactions were carried out under identical conditions except that the amount of 1-vinylperylene or perylene was varied. Purified monomer (25 mmole) was refluxed under nitrogen with AIBN (0.1 mmole) and the specified amount of 1-vinylperylene or perylene in benzene (7 ml) for 12 h. Poly(styrene) was precipitated by ethanol, poly(4-vinylpyridine) precipitated during the reaction, and the other two polymers were obtained by the removal of solvents at reduced pressure.

3.4 Conclusions

1-Vinylperylene has been shown to be an inhibitor instead of a polymerizable monomer. It inhibits the radical polymerization of styrene, 4-vinylpyridine, methyl methacrylate and vinyl acetate. The low reactivity of the monomer radical 3.1 may account for this inhibitory effect.

CHAPTER 4
SYNTHESES AND CONDENSATION POLYMERIZATIONS
OF PYRENYL MONOMERS

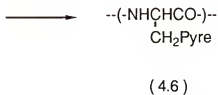
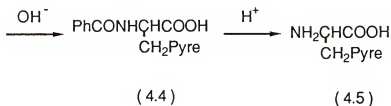
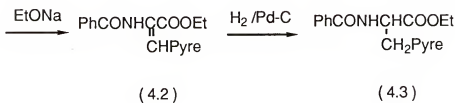
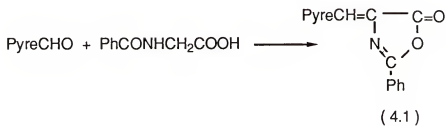
4.1 Introduction

In sharp contrast to the free radical polymerizations discussed in Chapter 2, the syntheses of polymers bearing pendant polycyclic aromatic groups have been rarely investigated by condensation polymerizations. This is probably due to difficulties in obtaining monomers of a sufficient purity and the requirement of high reaction conversions. Condensation polymerization is known to be very sensitive to the presence of impurities, and it can be seen from Equation 4.1 that a reaction of 90% conversion ($x=0.9$) could only yield 10 as the maximum degree of polymerization (X_n) [70MI69].

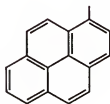
$$X_n = \frac{1}{1-x} \qquad \text{EQUATION 4.1}$$

An example of such polymerization, however, was reported in 1985, in which poly(pyren-1-ylmethylalanine) was prepared as shown in Scheme 4.1 [85MA882]. It can be seen that the synthetic procedures were quite lengthy and tedious. Furthermore, since its homopolymer would not

Scheme 4.1
Condensation Polymerization of Pyrenyl Monomer



Pyre:



dissolve in any solvent, the property tests were done on a block copolymer with γ -benzyl glutamate.

Our aim was to investigate the relationship between the optical effects and the distance of separation of pyrene units within the polymeric chain. It is desirable that the separations are exact, i.e. the x in Figure 4.1 has a series of definite lengths.

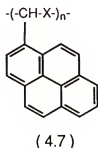


Figure 4.1.

The best method available to achieve this is by condensation polymerization, since the separation in this case can be simply manipulated by the number of atoms in the monomer chain. Radical homopolymerization of vinyl monomers gives a separation of one atom, whereas use of the technique of copolymerization results in a statistical separation except in the extreme case of alternating copolymerizations. The latter requires that the comonomers possess strong electron withdrawing groups and has not been well studied. Furthermore, poly(1-vinylpyrene)(PVP) sometimes has a high degree of crystallinity caused by the side chain-side chain interactions of bulky pendant groups [86MA2390]. This undesired characteristic is known to

interfere with the testing of some optical effects in the solid state and can be avoided in condensation polymers where the pyrene units can be suitably separated.

Table 4.1
Comparison of Requirements for Low Temperature and Melt
Polycondensation Methods [65MI1]

monomer	low temp. methods	melt methods
Purity	Moderate to High	High
Stoichiometric equivalence	Often tolerant of wide deviation	Necessary
Stability	Unnecessary	Necessary
Structure	Limited by reactivity requirement	Limited by thermal stability
<u>Polymerization Conditions</u>		
Time	Min. to h.	1-24 h.
Temp.	Normal	>200°C
Pressure	Atmospheric	High or low
Equipment	Normal	Special
<u>Products</u>		
Yield	Varies	High
Structure	Wide range	Limited by stability
By-products	Salt or none	Volatile org. compounds

Polycondensations can generally be classified in two categories as illustrated in Table 4.1. Apparently, the low temperature process, which deals with highly reactive

monomers, possesses great experimental advantages over the melt method in terms of speed and simplicity of equipment. Therefore, diol monomers with pyrene pendant groups are synthesized and polymerized with diisocyanates by this method in this chapter.

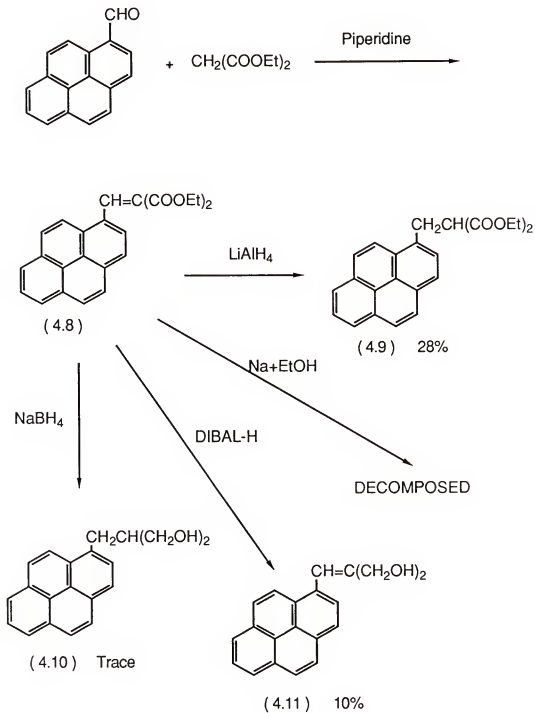
4.2 Results and Discussion

4.2.1 Syntheses of Monomers

No general synthesis of dihydroxy- or diamino-monomers is yet known. Diisobutylaluminum hydride (DIBAL-H) has been reported to reduce diethyl fumarate into trans-2-butene-1,4-diol in 65-70% yield [59JOC627]. This procedure was followed in an attempt to reduce diethyl pyren-1-ylmethylidenepropanedioate (4.8), prepared by the condensation of pyrene-1-carboxaldehyde and diethyl malonate (catalyzed by piperidine), to the corresponding diol as shown in Scheme 4.2. However, the yield was only 10% and no other reducing agents investigated were successful. Lithium aluminum hydride gave the saturated ester 4.9 in a low yield with the ester groups untouched, NaBH_4 resulted in a trace amount of the reduced diol 4.10, and metallic sodium in absolute ethanol decomposed the compound.

Pyren-1-ylmethylidenemalononitrile (4.12), synthesized from malononitrile and pyrene-1-carboxaldehyde by a similar method to the preparation of 4.8, is a red solid with a melting point of 255-256°C (Scheme 4.3). It is sparingly

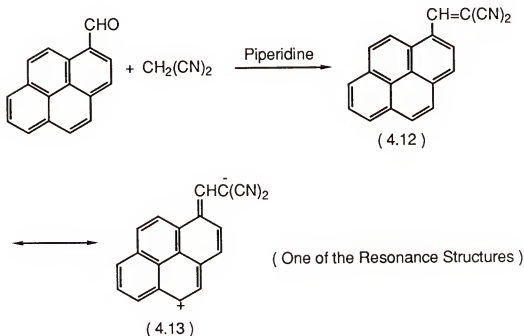
Scheme 4.2
Attempted Preparation of Diol Monomers



soluble in most solvents and also resisted reduction to the diamine. The four characteristic UV absorption bands of pyrene at 336, 321, 274 and 263 nm were not observed in its UV spectrum. Instead, a broad absorption peak stretching from 350 to 510 nm, centered at 440 nm, becomes the strongest band over 250 nm. This is similar to the reported charge transfer complex band for pyrene-TCNQ, which occupies the 500 to 730 nm region [62JCP457].

The hydroboration-oxidation of N-pyren-1-ylmethyl-diallylamine, following the reported procedure [78MI375] using BH_3 and H_2O_2 , failed to give the desired derivatives either.

Scheme 4.3
Preparation of Dicyanovinylpyrene

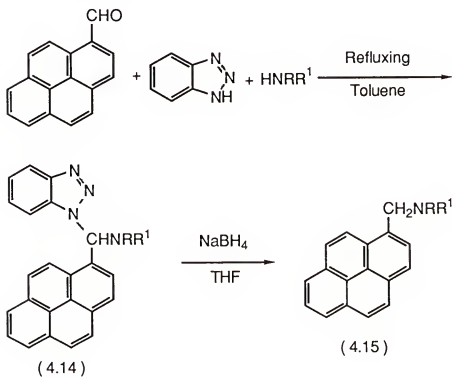


Previous work in our group has shown that benzotriazole can form a Mannich type adduct with an aldehyde and a secondary, or hindered primary, amine. The benzotriazole residue can be easily displaced from these adducts by nucleophiles [87JCS(P1)791]. As shown in Scheme 4.4, the intermediate compounds 4.14a and 4.14b, which were obtained quantitatively from diethanolamine and from 2-amino-2-methyl-1,3-propanediol, were reduced in situ using NaBH_4 in THF. The benzotriazole was easily removed to give the required products 4.15a and 4.15b. The yields of both reactions were over 80% based on the aldehyde and, since the reductions were carried out at room temperature, no formation of pyrene as a by-product was detected. The decomposition of pyrene derivatives to pyrene has been found in most of our reductions carried out at elevated temperatures.

The two ester groups in diethyl pyren-1-ylmethylidene-propanedioate (4.9) and the two hydroxymethyl groups in 2-(pyren-1-ylmethylidene)-1,3-propanediol (4.11) are both rendered distinct in their NMR spectra by the pyrene substituent. The chemical shift difference in the decoupled ^{13}C spectrum (75 MHz) is as great as 4.95 ppm for the two methylene groups in (4.11). The methylene group which is cis to the pyrene substituent may have been deshielded by the large aromatic ring current, and therefore resonanced at a lower field than its counterpart. Apparently, the substituents attached on the pyrene unit have experienced the electronic effect of the aromatic

system. On the other hand, the introduction of the branches may have little perturbational effect on the pyrene aromatic system itself as the UV spectra of the monomers are virtually the same as that of pyrene except for small difference in their molar absorption coefficients. The understanding about the interactions between the pyrene unit and its branches is important since the polymeric effect can thus be clearly distinguished when these monomers are polymerized.

Scheme 4.4
Preparation of Addition Monomers



4.15a. $R=R^1 = -CH_2CH_2OH$

4.15b. $R=H$; $R^1 = -\underset{\text{CH}_3}{\underset{|}{C}}(CH_2OH)_2$

4.2.2 Polymerizations

Melt polymerization was not a suitable method in this study due to the instability of the pyrene monomers. Organic diisocyanates were chosen as the comonomers since they are known to form addition polymers with diols at relatively low temperatures [60JPS49]. The polycondensations are exemplified in Scheme 4.5 with Entry 1 of Table 4.2. The molecular weights and polydispersities of the polymers prepared from N-(pyren-1-ylmethyl)diethanolamine (4.15a) and diisocyanates, as well as their polymerization conversions, are summarized in Table 4.2. It is remarkable that the molecular weight distributions of these addition polymers are quite

Scheme 4.5
Condensation Polymerization

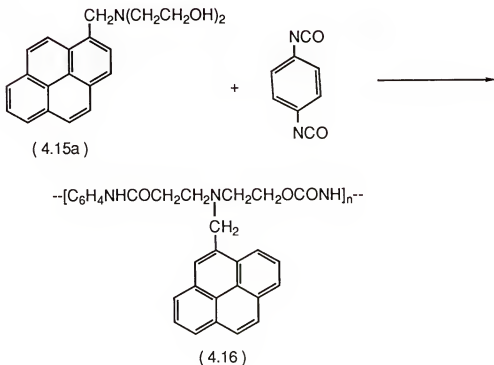


Table 4.2
Preparation of Condensation Polymers

	monomers		conversion %	M_w	M_w/M_n
	diols	diisocyanates			
4.15a		1,4-phenylene diisocyanate	96.0	24,000	1.7
4.15a		tolylene 2,4-diisocyanate	73.6	6,000	1.71
4.15a		bis(4-isocyanato-phenyl)methane	94.8	10,400	1.91

narrow, in the range of $M_w/M_n = 1.7$ to 1.9 . The relatively low polymerization conversion and low molecular weight of the polymer from tolylene 2,4-diisocyanate and 4.15a can possibly be attributed to the steric crowding of this diisocyanate. For 2-methyl-2-(pyren-1-ylmethyl)amino-1,3-dipropenediol (4.15b), however, no reasonable molecular weight polymer could be obtained by reaction with the same diisocyanates, even when dibutyltin dilaurate was used as the catalyst. Steric hindrance of this monomer may be the reasonable explanation of its low reactivity.

The structures of the polymers were characterized by IR and NMR spectroscopic methods. The IR spectra of the polymers displayed broad urethane carbonyl bands in the region around 1700 cm^{-1} . The typical isocyanate absorption band, which should occur in the region 2000 to 2300 cm^{-1} , was not observed in the IR spectra of the polymers. Demonstrated in Figure 4.2 is the proton decoupled ^{13}C NMR

spectrum of the polymer 4.16 recorded at 90°C. The spectrum clearly displayed the urethane carbonyl atom, resonanced at 153.6 ppm, and the three aliphatic carbon atoms. The aromatic region is apparently filled by the resonances of the pyrenyl and the phenyl carbon atoms. However, the NMR spectrum of this polymer observed at room temperature is more complicated than the one shown in Figure 4.2. Restricted rotation of the chain segment, and the orientation the of pyrene residues may explain the complication.

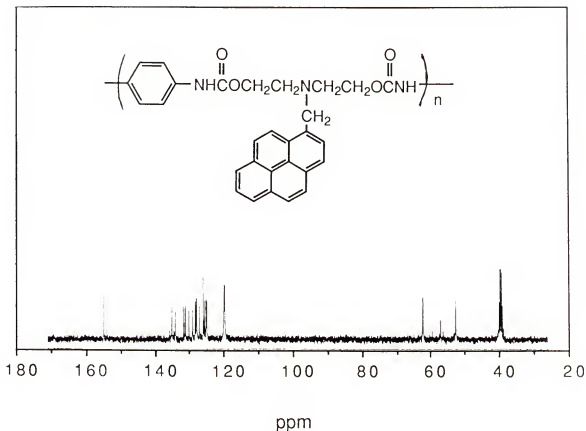


Figure 4.2. Proton decoupled ^{13}C NMR Spectrum

The photophysical properties of the polymers are similar to those of the diluted pyrene solution, which displays only the monomeric fluorescence of pyrene. Apparently, due to the remote separation of the pyrene units in the polymer chain, the chromophores do not interact with each other, which is the opposite case to poly(1-vinylpyrene).

The polymers are pale yellow powders and sparingly soluble in organic solvents, except DMSO, THF and DMF. The T_g s of the polymers are around 100 to 135°C.

4.3 Experimental Section

Pyrene-1-carboxaldehyde was synthesized by Vilsmeier's reaction [68BCJ2719]. Commercial phenylene 1,4-diisocyanate was purified by sublimation, mp.100-101°C. Bis(4-isocyanatophenyl)-methane, tolylene 2,4-diisocyanate, DMSO and 3,3-dimethyl-2-butanone were freshly distilled before use.

4.3.1 Preparation of Diethyl Pyren-1-ylmethylidenepropanedioate (4.8)

Pyrene-1-carboxaldehyde (9.2 g, 40 mmol) and diethyl malonate (6.6 g, 41 mmol) were dissolved in toluene (200 ml). Piperidine (0.5 g) was added and the mixture was refluxed under a Dean-Stark trap until the calculated amount of water had separated (about 2 h.). The solvent was evaporated close to dryness in vacuo and the residue diluted with 95% ethanol (100 ml). Upon standing overnight

at room temperature, crystals formed which were filtered off and subsequently purified by recrystallization from ethanol-dichloromethane(95:5) (12.5 g, 80.1% yield, mp. 111-113°C. Lit: 114°C [37AC(R)1]). NMR: ^1H (δ ppm/TMS): 8.71, s, 1H; 7.92-8.22, m, 9H (aromatic); 4.41, q, 2H; 4.21, q, 2H; 1.40, t, 3H; 1.07, t, 3H; ^{13}C (δ ppm/ CDCl_3): 166.9 and 164.5 (CO); 141.5; 132.8; 131.3; 130.8; 130.0; 128.9; 128.8; 127.5; 127.4; 126.5; 126.3; 126.2; 126.0; 124.8; 124.7; 124.5; 123.2 (aromatic and double bond); 61.86 and 62.08 (CH_2); 14.59 and 14.13 (CH_3). Analysis: for $\text{C}_{24}\text{H}_{20}\text{O}_4$ calculated: C:77.40, H:5.41; found: C:77.24, H:5.42.

4.3.2 Preparation of 2-(Pyren-1-ylmethylidene)propane-1,3-diol (4.11)

DIBAL-H (27 ml of 1.5M solution in toluene) was added over 30 min. to a stirred solution of compound 4.8 (3.70 g, 10 mmol) and benzene (10 ml) under nitrogen. The addition temperature was maintained below 50°C by a cool water bath. After standing overnight at room temperature, the reaction mixture was diluted with THF (30 ml) and quenched by the addition of methanol (5 ml), followed by water (2 ml). The mixture was filtered and the aluminum salts were washed several times with THF. The combined organic solvents were evaporated at reduced pressure, and the residue was recrystallized from toluene to yield the required product (0.30 g, 10.4% yield, mp. 165-166°C). NMR: ^1H (δ ppm/TMS): 8.32-8.05, m, 9H (aromatic); 7.40, s, 1H (CH=); 5.18, t, 1H

(OH); 4.93, t, 1H (OH); 4.45, d, 2H (CH₂); 4.14, d, 2H (CH₂); ¹³C(δppm/DMSO): 144.7; 131.9; 130.9; 130.4; 129.8; 128.3; 127.4; 127.3; 127.2; 127.0; 126.2; 125.2; 125.0; 124.5; 124.2; 123.9; 123.8; 122.3; 62.8; 57.9. Analysis: for C₂₀H₁₆O₂ calculated: C:83.31, H:5.59; found: C:83.03, H:5.61.

4.3.3 Preparation of Diethyl Pyren-1-ylmethylpropanedioate (4.9)

Compound 4.8 (1.90 g, 5.0 mmol) in THF (20 ml) was added to LiAlH₄ (0.19 g, 5.0 mmol) in THF (10 ml) over 2 h. under nitrogen. After refluxing for 5 h, the reaction was quenched by the addition of CH₃OH (5 ml). It was filtered with Celite and the filtrate was evaporated in vacuo. The product was finally obtained by recrystallization from propan-2-ol, with a little dichloromethane added (0.56 g, 28%, mp. 80-82°C). NMR: ¹H(δppm/TMS): 7.89-8.29, m, 9H (aromatic); 4.14, q, 4H (CH₂); 3.96, m, 3H (CH₂, CH); 1.16, t, 6H (CH₃). ¹³C(δppm/CDCl₃): 169.0 (CO), 131.7, 131.3, 130.7, 130.5, 128.8, 127.9, 127.8, 127.4, 127.0, 125.9, 125.2, 125.1, 125.0, 124.8, 124.7, 122.7 (aromatic), 61.5 (CH₂), 53.5 (CH), 32.2 (CH₂), 13.9 (CH₃). Analysis: for C₂₄H₂₂O₄ calculated: C:76.99, H:5.92; found: C:76.96, H:5.90.

4.3.4 Preparation of Pyren-1-ylmethylidenemalononitrile (4.12)

Pyrene-1-carboxaldehyde (9.2 g, 40 mmol), malononitrile (2.64 g, 40 mmol) and piperidine (0.5 g)

were dissolved in toluene (200 ml) and heated to reflux. A red precipitate formed immediately and was filtered off. Recrystallization from xylenes afforded the crystalline product as fine needles (7.8 g, 65.8%, mp. 254-255°C). Mass spectrum: 278 (100, M^+); 251 (35, $M^+ - \text{HCN}$); 139 (20, C_{11}H_7); 125 (55, C_{10}H_5); 112 (55, C_9H_4). NMR: ^1H (δ ppm/TMS): 9.45, s, 1H; 8.07-8.71, m, 9H (aromatic and CH=). ^{13}C (δ ppm/DMSO): 158.6; 134.4; 130.4; 130.3; 129.7; 129.6; 127.0; 126.9; 126.8; 125.5; 124.4; 123.4; 122.9; 122.4; 106.1 (not all the peaks appeared in the spectrum due to the insolubility of this compound). Analysis: for $\text{C}_{20}\text{H}_{20}\text{N}_2$ calculated: C:86.31, H:3.62, N:10.07; found: C:86.37, H:3.56, N:10.16.

4.3.5 Preparation of N-(Pyren-1-ylmethyl)diethanolamine (4.15a)

Pyrene-1-carboxaldehyde (11.4 g, 50 mmol), benzotriazole (6.0 g, 50 mmol) and diethanolamine (5.3 g, 50 mmol) were dissolved in toluene (250 ml) and refluxed in a Dean-Stark trap until 0.9 ml of water was collected. The toluene was evaporated under reduced pressure, and NaBH_4 (1.9 g, 50 mmol) in THF (100 ml) was added slowly to the residue cooled in ice water. The solution was stirred at room temperature overnight to ensure the complete removal of the benzotriazole group. Water was added and the solvents were evaporated. The residue was extracted with CHCl_3 and washed with aqueous NaOH to remove the remaining benzotriazole. The dried crude product from the organic

phase was further purified by recrystallization from benzene-hexanes (13.5 g, 84.5%, mp. 118–120°C). NMR: ^1H (δ ppm/TMS): 8.31, d, 1H and 7.7–8.1, m, 8H (aromatic); 4.12, s, 2H (CH_2); 3.37, t, 4H (CH_2); 3.18, bs, 2H (OH); 2.57, t, 4H (CH_2); ^{13}C (δ ppm/ CDCl_3): 131.4; 130.6; 130.3; 130.1; 129.1; 127.8; 127.6; 127.1; 126.8; 126.6; 125.3; 124.6; 124.1; 124.1; 123.9; 122.6 (aromatic); 59.0 (CH_2); 57.4 (CH_2); 55.4 (CH_2). Analysis: for $\text{C}_{21}\text{H}_{21}\text{NO}_2$ calculated: C:78.97, H:6.63, N:4.39; found: C:79.25, H:6.68, N:4.24.

4.3.6 Preparation of 2-Methyl-2-(pyren-1-ylmethyl)amino-propane-1,3-diol (4.15b)

The reaction procedure was the same as for 4.15a above, except that after washing with aqueous NaOH, followed by water, the product precipitated from the CHCl_3 solution. The pure product was obtained by recrystallization from ethyl acetate (82.7%, mp. 138–139°C). NMR: ^1H (δ ppm/TMS): 9.04, d, 1H and 8.78–8.55, m, 8H (aromatic); 5.15, bs, 3H (NH,OH); 4.91, s, 2H (CH_2); 4.02, s, 4H(CH_2); 1.68, s, 2H (CH_3); ^{13}C (δ ppm/DMSO): 135.6; 130.8; 130.4; 129.8; 128.5; 127.4; 127.3; 127.1; 126.7; 126.0; 124.9; 124.8; 124.7; 124.1; 124.0; 123.8 (aromatic); 64.7 (CH_2); 57.4 (CH_2); 43.4 (C); 16.6 (CH_3). Analysis: for $\text{C}_{21}\text{H}_{21}\text{NO}_2$ calculated: C:78.97, H:6.63, N:4.39; found: C:78.95, H:6.72, N:4.33.

4.3.7 Addition Polymerizations

All the polymerizations were carried out under the following reaction conditions: 4.15a (3.2 g, 10.0 mmol) was dissolved in DMSO (10 ml) and added to a rapidly stirred solution of diisocyanate (10.0 mmol) in methyl isobutyl ketone (10 ml). After heating at 110-120°C for 2h. the clear solution was poured into 95% ethanol (50 ml) to precipitate the polyurethane. The polymer was washed with ethanol and dried in vacuo at 80°C.

4.4 Summary

Polymers bearing remotely separated pyrene units have been prepared by addition polymerizations of diisocyanate and dihydroxy monomers. The functional monomers were prepared by using benzotriazole as an auxiliary, whereas the reduction of corresponding diester compounds failed to afford the expected monomers. The photophysical properties of these polymers are similar to that of the dilute pyrene solution, showing no excimer emission.

CHAPTER 5
Formylation of Pendant Aromatic Groups
Attached to Linear Polymer Chains

5.1 Introduction

Formylation of pendant aromatic groups has been a key step in the functionalization of many polymers. The aromatic aldehyde which results is highly reactive and can be used as a site for further synthetic manipulations. However, in contrast to its importance, there are few methods for the formylation of these polymers, and these all relate to crosslinked polystyrene and to formylation by multiple step processes such as, bromination, lithiation and then quenching with dimethylformamide [76JOC3877], or chloromethylation followed by the oxidation using dimethyl sulfoxide [75JCS(C)225]. No formylations of linear polymers have been reported.

Although *p*-formylstyrene is commercially available and can undergo free radical polymerization to afford the linear *p*-formylstyrene polymer [74JPS(C)2449], the syntheses of functional monomers with larger formylated aromatic substituents have not been reported. The preparations of such monomers appear to be difficult, therefore, the formylation of readily available poly(1-vinylaromatics) is an attractive method of approach.

The chief objective of the present study is to develop a general formylation method for such polymers. Most of the attention has focused on linear products, which may then be studied in solution or altered by further reactions.

5.2 Abbreviations

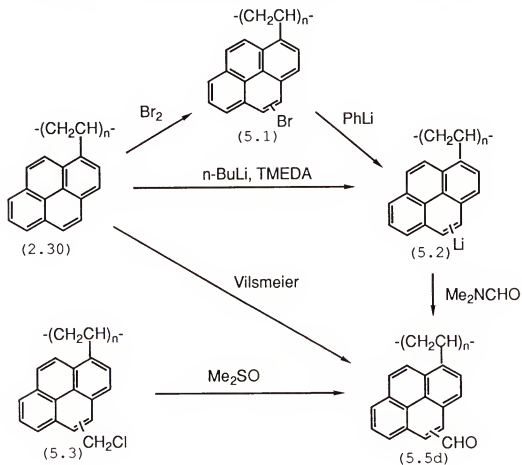
Formylated poly(1-vinylpyrene) (PVP), polystyrene (PS), poly(1-vinylnaphthalene) (PVN) and poly(9-vinylphenanthrene) (PVPh) are abbreviated to PVP-CHO, PS-CHO, PVN-CHO and PVPh-CHO, respectively. Meanwhile, P-CHO is designated as the general term for these types of polymers. The reaction products of formylated polymers with propanedinitrile are similarly abbreviated to PVP-CH=C(CN)₂, PS-CH=C(CN)₂, PVN-CH=C(CN)₂ and PVPh-CH=C(CN)₂, accordingly. In like manner, P-CH=C(CN)₂ becomes the general term for this class of polymers.

5.3 Results and Discussion

Crosslinking during reactions of linear polymers is a common phenomenon due to the short separation between two functional groups in the polymeric chain. In many cases, the mechanism of the crosslinking reaction remains unknown. Only crosslinked polymer could be obtained when formylation of PVP was attempted as shown in Scheme 5.1 [76JOC3877, 75JCS(C)225]. Direct lithiation of the polymer, a reported

method for the lithiation of linear polystyrene [74JPS(C)247], was not possible since PVP is not soluble in hexane. Treatment of the brominated polymers with phenyllithium or butyllithium resulted in insoluble products. The oxidation of chloromethylated PVP (PVP-CH₂Cl) was also not useful due to the difficulty in preparing linear PVP-CH₂Cl with an appreciable amount of substitution. The Vilsmeier reaction [38JA2555], another frequently used method for the formylation of aromatics, failed to formylate the PVP at room temperature and decomposed the starting material at higher temperatures.

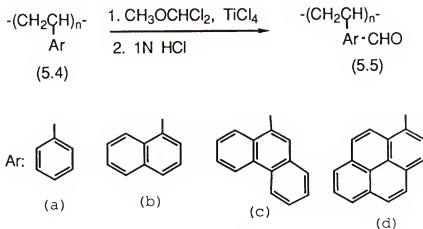
Scheme 5.1
Attempted Formylation of Poly(1-vinylpyrene)



The use of dichloromethyl butyl ether and titanium(IV) chloride as formylating reagent for coronene has been reported [67T985]. The high reactivity of the reagents, and the easy hydrolysis of the dichloromethyl substituent introduced, enabled the formylation to be completed in a short time under very mild conditions, thus minimizing the crosslinking (Scheme 5.2).

Evidence that formylation of the polymers has indeed taken place is as follows. Strong carbonyl absorption bands (ranging from 1670 to 1700 cm^{-1}) and broad aldehyde proton peaks (centered at 10.5 ppm), are observed in the IR spectra and the NMR spectra of all the products. These absorptions are not present in the starting polymers. The formylated polymers react with $\text{CH}_2(\text{CN})_2$, and the IR spectra of these products show intense nitrile absorptions around 2230 cm^{-1} (Figure 5.1). All polymer products give good

Scheme 5.2
Formylation of Linear Polymers



elemental analysis results for their corresponding structures.

The ^1H NMR spectrum of a PVP-CHO sample, prepared under the conditions described in the Experimental Section, is illustrated in Figure 5.2. The resonance around 9 ppm is the proton from a pyrene unit, which is observed as a doublet at 8.87 ppm in pyrene-1-carboxaldehyde.

The polymers in Table 5.1, with the exception of PS, were obtained under the conditions described in the Experimental Section. Formylation of PS was carried out with a longer reaction time than the other polymers. The degree of formylation of the polymers given in Table 5.1 is defined as the percentage of repeating mono- or polycyclic aromatic units which are formylated. This percentage was estimated from the comparison of the integrations of the

Table 5.1
Results of Polymer Formylation

polymer	$M_w \times 10^{-3}$	M_w/M_n	IR(C=O) cm^{-1}	degree of formylation% ^a	yield % ^b
PS-CHO	16.5	1.22	1695	27	45
PS-CHO(Cross-linked) ^c			1695	~20	
PVN-CHO	11.2	1.06	1678	56	65
PVPh-CHO	11.8	1.22	1684	45	78
PVP-CHO	15.2	1.23	1672	58	92

^a Determined from ^1H NMR except for cross-linked PS-CHO, which is estimated from its IR spectrum. ^b Based on the recovered linear products. ^c Polystyrene-2% divinylbenzene copolymer beads (200-400 mesh).

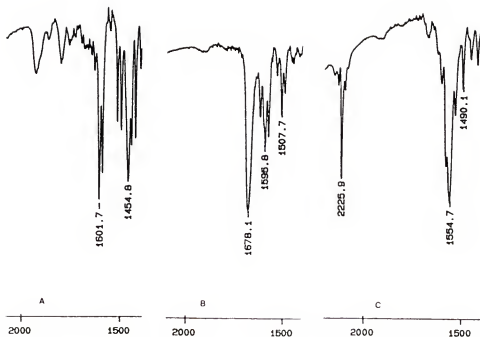


Figure 5.1. IR spectra of PVP (A); PVP-CHO (B, 71% substituted); PVP-CH=C(CN)₂ (C, derived from B).

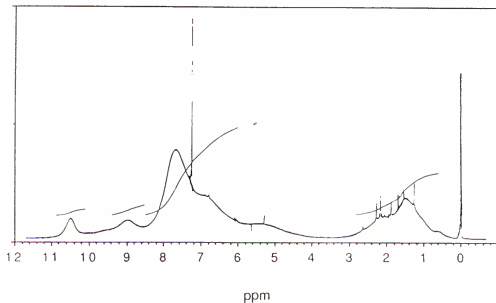


Figure 5.2. ¹H NMR of PVP-CHO (49% substituted) in CDCl₃ at room temperature.

aldehyde and the aromatic protons. Polymers bearing condensed aromatics can be functionalized to a very high degree without crosslinking by increasing the ratio of reagents. In other words, the degree of functionalization for condensed aromatic polymers can be controlled. As is indicated in Figure 5.3, the degree of substitution of PVP could be varied by the use of different molar ratios of reagents, although the overall yield was found to decrease with an increasing degree of substitution. In the case of PS, attempts to raise the degree of substitution by increasing the reaction time or the ratio of the reagents resulted in crosslinking of the polymer. The relatively low substitution of PS may be accounted for by the low reactivity of the phenyl group towards electrophilic substitution, relative to the reactivity of the polycyclic

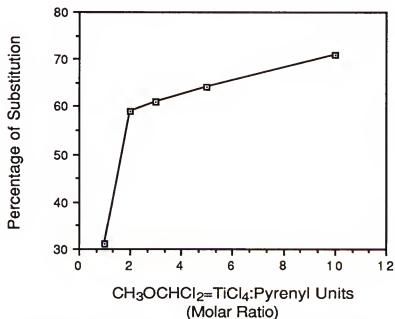


Figure 5.3. Dependence of PVP substitution on the amount of reagents used.

larger aromatic systems. Alternatively, highly substituted PS-CHO can be obtained by the polymerization of p-formylstyrene [74JPS(C)2449]. Notably, the yields in Table 5.1 increase with the size of the aromatic functional group.

Moderate molecular weight polymers were used in the present study, as is shown in Table 5.1. The effect of molecular weight was investigated using PS. The formylation of PS becomes more difficult as the molecular weight increases. The yields of the formylated PS decrease with higher molecular weight samples due to the longer reaction times required, leading to more crosslinked product. However, for the polymers with condensed aromatic groups, high molecular weight is better tolerated in their formylation reactions than for PS. The high reactivity of the condensed aromatic ring allows high molecular weight samples to be formylated in times sufficiently short to avoid the crosslinking reaction. An example of this was that a reasonable yield (78%) of highly substituted PVP-CHO was prepared in a few minutes using a molar ratio of $\text{CH}_3\text{OCHCl}_2\text{:TiCl}_4\text{:Pyrene Units}$ of 10:10:1. However, PS of comparable molecular weight under the same conditions was formylated only if it was reacted for a much longer time.

The solubility characteristics of the formylated polymers are listed in Table 5.2. The PVP-CHO listed there is the 58% substituted sample from Table 5.1. For the PVP-CHOs in Figure 5.2, the general solubility is in the reverse order of the degree of substitution. For instance,

a 31% formylated sample of PVP-CHO is soluble in nearly all the solvents listed in Table 5.2, whereas the 71% substituted sample is soluble only in CS_2 and CHCl_3 . The appreciable solubility of these formylated polymers in organic solvents makes them highly useful intermediates for further modifications and for property studies.

Table 5.2
Solubility of Formylated Polymers

polymer	Solvents						
	CHCl_3	THF	DMF	DMSO	$\text{C}_6\text{H}_5\text{CH}_3$	$\text{C}_6\text{H}_5\text{Cl}$	CS_2
PS-CHO	Y	Y	Y	P	Y	Y	Y
PVN-CHO	Y	Y	Y	P	Y	Y	Y
PVPh-CHO	Y	Y	Y	Y	Y	Y	Y
PVP-CHO	Y	P	Y	N	N	N	Y

Y: soluble; N: insoluble or sparingly soluble; P: partially soluble. Conditions: 0.05 g of polymer in 5.0 ml solvent at room temperature.

Significantly, this formylation method works well not only for linear but also for crosslinked polymers, as is illustrated by the result of crosslinked PS (Table 5.1). Besides the advantage that the PS-CHO is obtained in one step, as compared with the reported multiple step preparations [76JOC3877, 75JPS(C)225], it is reasonable to assume, from the results of linear polymers, that the product has undergone little additional cross-linking. Therefore, PS-CHO prepared in this way should possess a

similar degree of crosslinking and porosity as that of the starting material, and the aldehyde group should react rather completely in its further reactions. It is well-known that the inaccessibility of functionality created by additional crosslinking reduces their reactivity.

All the P-CHOs reacted readily with propanedinitrile in the presence of a catalytic amount of piperidine. The completion of the reactions was indicated by the disappearance of the strong carbonyl absorption band at 1670-1700 cm^{-1} and the presence of 2230 cm^{-1} nitrile absorption in the IR spectra of the products. The P-CH=C(CN)₂ polymers are colored due to the extended conjugation. With the presence of the interesting charge transfer absorption band centered at 450 nm, the UV spectrum of a highly substituted PVP-CH=C(CN)₂ is very similar to that of the 1-pyrenylmethylenepropanedinitrile [80MI199].

5.4 Experimental Section

5.4.1 Preparation of Polymers

The vinyl monomers were prepared as described in Chapter 2. Their polymerizations were carried out at 60°C under N₂ in dry toluene with AIBN as initiator. The polymers were precipitated from solution by the addition of ethanol. The residual monomer was removed by refluxing with ethanol in a Soxhlet overnight. It was found that

poly(1-vinylpyrene), when initially precipitated from its polymerization solution, could contain as much as 20% residual monomer.

5.4.2 Formylation of Polymers

All the polymers were formylated by the same general procedure. A typical formylation of PVP is given as an example. 1,1-Dichloromethyl methyl ether (0.94 ml, 10 mmol) was added to a solution of PVP (1.14 g, 5.0 mmol) in CS_2 (100 ml). Titanium(IV) chloride (1.1 ml, 10 mmol) was then injected and the yellow solution darkened immediately. The mixture was stirred at room temperature for one hour and was then decomposed by the addition of 1N HCl (50 ml). The CS_2 was removed by distillation, and the polymer was filtered off, washed with water, ethanol and finally ammonia. The crude PVPPh-CHO was further purified by reprecipitation from its clear chloroform solution with ethanol. The final product (1.17 g) was obtained as a pale yellow powder after drying in a vacuum oven at 60°C overnight.

5.4.3 Reaction of Formylated Polymers with $\text{CH}_2(\text{CN})_2$

In a typical reaction, propanedinitrile (0.1 g, 1.5 mmol) was added to a formylated polymer (0.1 g, <1.0 mmol) in chloroform (25 ml), followed by the addition of a catalytic amount of piperidine. The reaction was stirred at room temperature for one hour and the precipitated polymer filtered off. If the polymer did not precipitate,

95% ethanol was added to induce the separation. The crude polymer was purified by refluxing with acetone in a Soxhlet overnight.

5.5 Conclusion

The use of 1,1-dichloromethyl methyl ether and titanium(IV) chloride in carbon disulfide has proved to be a very good method for the formylation of both linear and crosslinked poly(1-vinylaromatics), especially for polymers bearing condensed aromatic substituents. Other reported methods are not suitable for the formylation of linear polymers due to the occurrence of crosslinking during the reactions. The mild reaction conditions and the short reaction time of the present method minimizes the formation of crosslinked polymers.

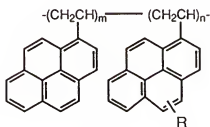
CHAPTER 6
SYNTHETIC AND PHOTOPHYSICAL INVESTIGATIONS
OF SUBSTITUTED POLY(1-VINYLPYRENE)

6.1 Introduction

The preparation and properties of poly(1-vinylpyrene) (PVP), a classic excimer-forming polymer, have been investigated extensively as has been shown in Chapter 2. Photophysical studies of PVP have examined triplet-triplet absorption spectra, excimer fluorescence [72JCP1746, 86MA2390, 72CL499, 85MA1366], and pulse-photoconductivity [87BCJ83]. Moreover, intramolecular exciplex formation in poly[(1-vinylpyrene)-co-(4-dimethylaminostyrene)] has also been reported [85JPS(C)585]. These investigations, together with studies of model compounds such as 2,4-di(1-pyrenyl)pentane[83MA1390] and [1-(1-pyrenyl)ethyl]ether [85MA1026], have provided an in depth understanding of the excited state behavior of PVP.

The focus of the present investigation, the synthesis and photophysics of substituted PVP (Figure 6.1), is an extension of the work on PVP. At the onset of the investigation it was envisaged that the photophysical properties of PVP would be dramatically altered by functionalization with either an electron-withdrawing or an electron-donating group. Such modifications should both

enhance the delocalization and change the distribution of the π electron clouds, and also increase their charge asymmetry which is essential for photo-active materials. Concurrent studies of substituted pyrene model compounds indicated that the absorption and emission properties of the pyrene chromophore are strongly influenced by the nature of the substituents. Furthermore, the presence of two chromophores in the same polymer backbone (pyrene and substituted pyrene units, see Figure 6.1), which would result from partial substitution of PVP, could give rise to interesting possibilities such as the formation of hetero-excimers between chromophores with different substituents. The degree of substitution, which can be controlled by varying the reaction conditions, can also play an important role in determining the photophysical properties of the polymers since it changes the ratio of the chromophores in the polymeric chain. As a result, both the emission and absorption spectra of a functionalized PVP may be complex owing to the presence of several inter-chromophore interactions: (i) energy transfer from a pyrene unit to a substituted pyrene unit;



(6.1)

Figure 6.1. General structure of substituted PVP.

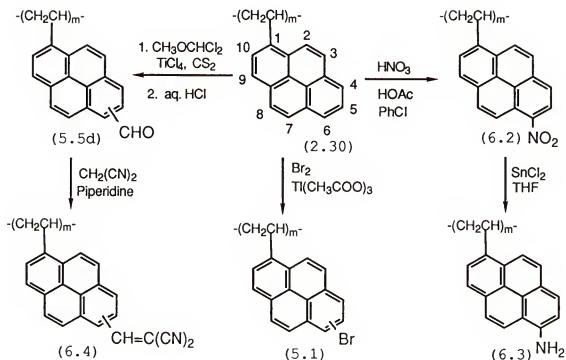
(ii) homo-excimer formation by interaction of two substituted pyrene units; (iii) hetero-excimer formation by interaction of a pyrene and a substituted pyrene. In addition, in several of the substituted PVP's, energetically low-lying intramolecular charge transfer (ICT) excited states dominate the photophysics of chromophores. Studies of model compounds indicate that the emission from the ICT state is strongly medium dependent, thus, owing to the unique microenvironments possible in the polymers, strong variation in the emission properties may be expected as a function of the solvation ability of solvents.

6.2 Results and Discussion

6.2.1 Syntheses of Polymers

Table 6.1 summarizes the polymers prepared according to Scheme 6.1. The polymers were characterized by their elemental analyses and IR spectra. GPC data revealed that the molecular weights remained virtually unchanged in the functionalized polymers obtained by chemical modification. Attention was focused on the obtaining of linear, functionalized polymers, which could then be studied photophysically in solution. Crosslinking occurs readily during chemical modification of PVP if conditions are not strictly controlled (the occurrence of crosslinking was indicated by a cloudiness or the formation of a precipitate in the reaction solution). For example, nitration of PVP

Scheme 6.1
Syntheses of Substituted PVP



to a high degree of functionalization could not be achieved owing to crosslinking under strong reaction conditions. The maximum degree of nitration obtained was approximately 50% as determined by elemental analysis (see Table 6.1).

No evidence of polysubstitution in the pyrene units was found, presumably due to the deactivating effects of the nitro, formyl and bromo groups in the polymers described in the present work.

The UV-visible absorption spectrum of nitrated poly(1-vinylpyrene) displays a broad band at $\lambda_{max} = 415$ nm; this is very similar to that reported for 1-nitropyrene. Since the UV-visible spectra of neither 2-nitropyrene

Table 6.1
Substituted Poly(1-vinylpyrene)

polymer ^a	degree of substitution, % ^b	elemental analysis	characteristic IR absorptions, cm ⁻¹
PVP-CHO (5.5d)	40	-----	1670(s), -CHO
PVP-NO ₂ (6.2)	49	2.75(N%)	1508(s), 1329(s), -NO ₂
PVP-NH ₂ (6.3)	30	1.83(N%)	1619(s), 3450(w), -NH ₂
PVP-Br (5.1)	42	12.72(Br%)	-----
PVP-CH=C(CN) ₂			
(6.4a)	40	4.30(N%)	2214(s), -CN
(6.4b)	74	7.29(N%)	2214(s), -CN
(6.4c)	88	8.39(N%)	2214(s), -CN
(6.4d)	99	9.18(N%)	2214(s), -CN

^a See Scheme 6.1 for detailed structures. ^b Percentage of functionalized pyrene units, obtained from elemental analysis except for PVP-CHO, which is estimated from that of the PVP-CH=C(CN)₂.

nor 4-nitropyrene have absorption above 400 nm [87RTC120], the structure shown in Scheme 6.1 is used to represent this polymer. Nitration at the 4- or 9-position of PVP would also yield a chromophore having a similar spectrum. However, these positions are less likely to be substituted because of steric hindrance by the polymeric chain.

The reduction of nitrated PVP (6.2) was initially carried out by using SnCl₂ and concentrated HCl in DMF, a method reported for the reduction of nitrated polystyrene to the corresponding amine [69B4728]. However, the IR spectrum of the PVP-NO₂ reduced in this manner exhibits a strong band at 1678 cm⁻¹ which is not observed in the

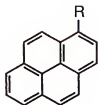
spectrum of 1-aminopyrene. Furthermore, reaction of this polymer with benzaldehyde and with benzoyl chloride resulted in the recovery of starting material. It is possible that the product of the SnCl_2 reduction is PVP-NHCHO, formed by the reaction of the polymeric amine with solvent DMF. PVP-NH₂ (6.3) was finally prepared by the reduction of PVP-NO₂ using SnCl_2 in THF. The IR spectrum of this product is now almost identical to that of a mixture of 1-aminopyrene and pyrene (1:1 in moles). Elemental analysis indicated that some of the nitrated pyrene units were reduced back to pyrene, affording a lower degree of substitution in PVP-NH₂ than in PVP-NO₂ (see Table 6.1). The presence of free pyrenylamino groups was verified by the preparation of a Schiff base, by heating with benzaldehyde at 80°C for 5 hours.

Bromination of PVP was catalyzed by $\text{Ti}(\text{OAc})_3$ [72JOC88]. Substitution is assumed to occur at the aromatic ring instead of at the aliphatic polymer chain because the reaction was carried out in dark, and since the IR spectrum of the brominated PVP is very similar to that of bromopyrene. The degree of substitution could be controlled up to 40% substitution by the amount of bromine which was added. A higher degree of substitution could not be obtained without the occurrence of an appreciable amount of crosslinking. A 50% yield of crosslinked polymer was obtained when the stoichiometric amount of bromine was used. Stronger Lewis acid catalysts, such as FeCl_3 , resulted in exclusive formation of crosslinked PVP-Br.

As shown in Scheme 6.1, PVP-CH=C(CN)_2 was prepared by the reaction of PVP-CHO with malononitrile in the presence of a catalytic amount of piperidine. The aldehyde group in polymer 5.5d was converted completely to the dicyanovinyl group as indicated by the IR spectrum of PVP-CH=C(CN)_2 which exhibits no presence of carbonyl band. Furthermore, the nitrogen analysis of the highly substituted PVP-CH=C(CN)_2 suggests quantitative functionalization (see Table 6.1).

6.2.2 Absorption Spectra

The absorption spectra of the polymers, along with the corresponding mono-substituted pyrene models (see figure 6.2 for structures), are displayed in Figure 6.3. Bromine has little effect on the absorption of PVP, the UV spectrum of a 40% substituted PVP-Br is identical to that of PVP. The absorption spectra of the other polymers are similar to those of mixture of pyrene and the corresponding mono-substituted pyrenes. The broad bands that occur to the red of the typical PVP absorptions (331 and 348, nm) arise from those of the substituted pyrene chromophores. The red shift and broadening of the absorption band due to



R: CHO; Br; NO₂; NH₂; CH=C(CN)₂

Figure 6.2. Structures of 1-substituted pyrenes.

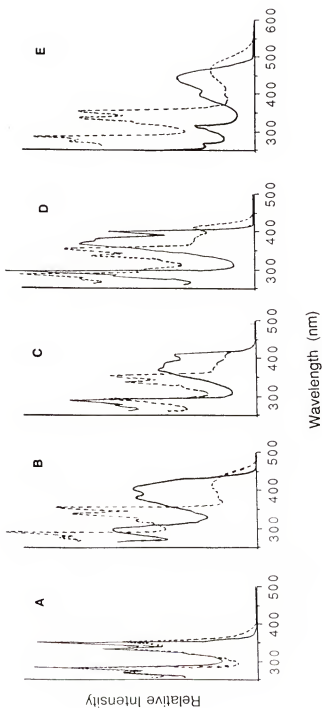


Figure 6.3. Absorption spectra of substituted PVP (---) and 1-substituted pyrene (---): (A) PVP-Br, PyreBr; (B) PVP-NO₂, PyreNO₂; (C) PVP-NH₂, PyreNH₂; (D) PVP-CH=C(CN)₂, PyreCH=C(CN)₂; (E) PVP-CHO, PyreCHO.

the substituted pyrene chromophore in the polymer (compared to the corresponding model compounds, see Figure 6.3) may be due to heterogeneity with respect to the conformation of the chromophore units and the microenvironments experienced by the chromophores in the polymer. In general, while there are subtle differences between the UV-visible spectra of the polymers and the corresponding model compounds, the overall similarity of the spectra suggest that ground-state inter-chromophore interactions do not occur in the polymers.

6.2.3 Effect of Solvent and Excitation Wavelength on Substituted PVP Fluorescence

Fluorescence maxima as a function of excitation wavelength in DMF and THF for the substituted PVP polymers and the corresponding 1-substituted pyrene compounds are summarized in Tables 6.2 and 6.3, respectively. Several representative excitation and fluorescence spectra are shown in Figures 6.4 - 6.7. Interestingly, the polymers display spectra which are strongly dependent on both the excitation wavelength and on solvent. In general, the fluorescence of the polymers is more sensitive to the polarity of the solvent medium than the fluorescence of the substituted pyrene models. For example, the position of the ICT emission of PVP-CH=C(CN)_2 red-shifts 40 nm on changing solvents from THF to DMF. By contrast, the fluorescence of the PyreCH=C(CN)_2 red-shifts only 25 nm for the same variation (Table 6.3). The enhanced sensitivity

Table 6.2
Fluorescence Data of Substituted Poly(1-vinylpyrene)^a

solvent	PVP-CHO (<u>5.5d</u>)	PVP-Br (<u>5.1</u>)	PVP-NO ₂ (<u>6.2</u>)	PVP-NH ₂ (<u>6.3</u>)	PVP-CH=C(CN) ₂ (<u>6.4a</u>)	(<u>6.4b</u>)	(<u>6.4c</u>)	(<u>6.4d</u>)
DMF	582(350)	492(350)	686(350) 500(350)	570(350)	705(350) 510(350)	705(350)	705(350)	600(350)
	582(407)		686(420)	580(410)	705(460)	705(460)	705(460)	705(460)
THF	560(350)	505(350)	640(350)	540(350)	665(350)	665(350)	665(350)	590(350)
	560(407)		640(420)	540(410)	665(460)	665(460)	665(460)	665(460)

^a Emission maxima in nm (excitation wavelength in nm)

Table 6.3
Fluorescence Data of 1-Substituted Pyrene^a

solvent	PyreCHO	PyreBr ^b	PyreNO ₂	PyreNH ₂	PyreCH=C(CN) ₂
DMF	415(350)	---(350)	---(350)	435(350)	528(350)
	415(390)		492(410)	435(400)	528(450)
THF	---(350)	---(350)	---(350)	427(350)	503(350)
	---(390)		---(410)	427(400)	503(450)

^a Emission maxima in nm (excitation wavelength in nm).
^b Only pyrene emission was observed.

of the polymer fluorescence to solvent may be due to the fact that solvent affects the conformation of the polymers. This in turn may have a strong influence on the microenvironment experienced by the chromophores and the degree of intra-chromophore interactions. Clear examples of the latter effect are observed for several of the substituted PVP's and will be discussed below.

The fluorescence spectrum of PVP-Br (40% brominated) is identical to that of the PVP showing no dependence on the excitation energy. The emission observed from this PVP-Br sample may arise purely from the excimer of unsubstituted PVP since it is known that bromopyrene undergoes non-radiative decay [68CPL535].

For PVP-CHO (5.5d), despite the fact that the polymer is only 40% formylated, the pyrene or pyrene excimer emission was not observed when the excitation wavelength

was set at the corresponding pyrene chromophore absorption. Furthermore, the emission spectrum is unaffected by the excitation wavelength in both DMF and THF (see Figure 6.4). These may suggest that energy transfer occurs with unit efficiency. Note that the occurrence of efficient energy transfer is supported by the clear observation of the pyrene absorption doublet in the the excitation spectrum of PVP-CHO fluorescence.

The position and bandshape of the fluorescence of PVP-NO₂ in THF (Figure 6.5A) is similar to the fluorescence of 1-nitropyrene, regardless of the excitation wavelength. This indicates that the fluorescence occurs from the

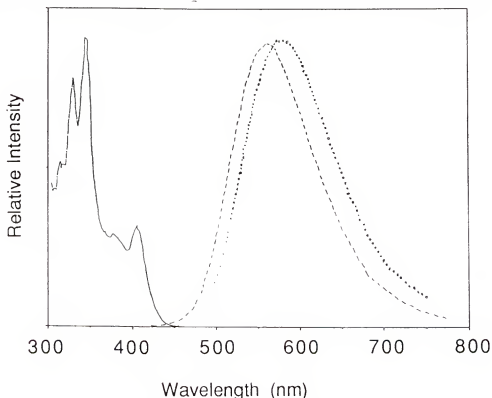


Figure 6.4. Fluorescence and fluorescence excitation spectra of PVP-CHO: (.....) fluorescence in DMF ($\lambda_{\text{ex}} = 350, 407$ nm, superimposed); (---) fluorescence in THF ($\lambda_{\text{ex}} = 350, 407$ nm, superimposed) in THF; (—) excitation in THF ($\lambda_{\text{em}} = 580$ nm).

pyrene-NO₂ chromophore. Note that excitation spectrum of the polymer clearly displays bands for both the pyrene and pyrene-NO₂ chromophores. Since the polymer is only 50% substituted (Table 6.1), these observations suggest that, for PVP-NO₂ in THF, energy transfer from the pyrene chromophore to the pyrene-NO₂ chromophore is highly efficient.

Interestingly, although the fluorescence and the fluorescence excitation spectra of PVP-NO₂ in THF are wavelength independent (Figure 6.5A), they become highly dependent in DMF (Figure 6.5B). Excitation of the polymer at a wavelength corresponding to the ICT absorption of the pyrene-NO₂ chromophore (420 nm) produces a single, long wavelength band (686 nm) which is characteristic of the ICT state. However, excitation at the pyrene chromophore wavelength (350 nm) results in the pyrene-NO₂ emission and a band at higher energy (500 nm). It is likely that the high energy fluorescence emanates from an excited state that is based on the unsubstituted pyrene chromophore, because it is very similar to the emission observed from unsubstituted PVP. As the fluorescence of PVP has been assigned to the pyrene homo-excimer, the high energy fluorescence from PVP-NO₂ in Figure 6.5B is tentatively assigned to this excited state.

The remarkable feature in the observation of pyrene-based fluorescence in DMF indicate that in this solvent interaction between the pyrene and pyrene-NO₂ chromophores is sufficiently weak, so that energy transfer is not highly

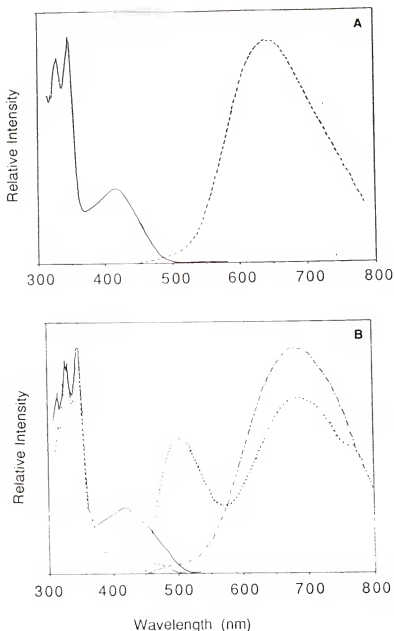


Figure 6.5. Fluorescence and fluorescence excitation spectra of PVP-NO₂. A: (—) excitation in THF ($\lambda_{em} = 600$ nm); (---) fluorescence in THF ($\lambda_{ex} = 350, 420$ nm, superimposed); (B) (---) excitation in DMF ($\lambda_{em} = 510$ nm); (—) excitation in DMF ($\lambda_{em} = 700$ nm); (.....) fluorescence in DMF ($\lambda_{ex} = 350$ nm); (----) fluorescence in DMF ($\lambda_{ex} = 420$ nm).

efficient. This contrasts with the situation in THF, where energy transfer apparently is very efficient. The solvent effect on energy transfer efficiency may arise from solvent-dependent conformations of the polymer. Qualitatively, PVP-NO₂ is more soluble in THF than in DMF; as a result, the polymer probably adopts a "less-extended" conformation in DMF compared to THF. Because of this, pyrene homo-excimer formation may be more likely in DMF. In addition, the coiled conformation in this rather viscous DMF solvent tends to form heterogeneous domains or

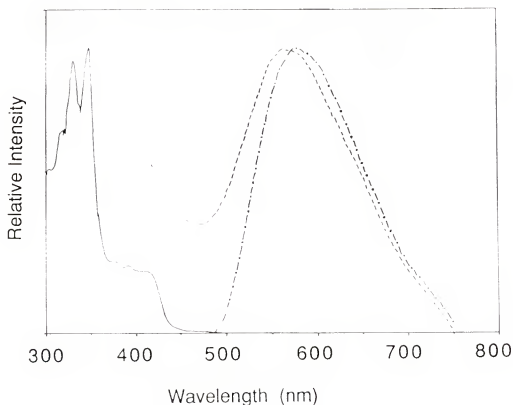


Figure 6.6. Fluorescence and fluorescence excitation spectra of PVP-NH₂ in DMF: (—) excitation (λ_{em} = 540 nm); (---) fluorescence (λ_{ex} = 350 nm); (-.-.-) fluorescence (λ_{ex} = 410 nm).

microphase separation within the polymer, which may decrease the efficiency of pyrene to pyrene-NO₂ energy transfer.

The fluorescence properties of PVP-NH₂ are similar to those observed for PVP-NO₂. The emission is independent of excitation wavelength for the polymer in THF solution, indicating that energy transfer among the chromophores is efficient. However, in DMF the fluorescence of PVP-NH₂ is strongly wavelength dependent. The emission is qualitatively similar to that of PVP-NO₂ in DMF, suggesting that for PVP-NH₂ in DMF the efficiency of energy transfer between the chromophores is also reduced compared to THF.

6.2.4 Degree of Functionalization

As indicated in Table 7.1, PVP-CH=C(CN)₂ was prepared with a degree of substitution ranging from 40% to nearly quantitative. Similar to the polymers discussed above (e.g. PVP-NO₂ and PVP-NH₂) incomplete energy transfer was observed for the polymer sample with the lowest degree of substitution (6.4a) in DMF (Figure 7.7 and Table 7.2). This conclusion is based on the fact that excitation of sample 5a at 350 nm produces two emission bands (510 nm and 705 nm). However, as the degree of substitution by the -CH=C(CN)₂ group increases, the high energy fluorescence band becomes less pronounced, even in DMF solution. Since the high energy band has been tentatively assigned to emission from the unsubstituted pyrene (excimer), this

observation suggests that as the degree of substitution increases, energy transfer from the unsubstituted chromophores to the substituted chromophores becomes efficient. Interestingly, the fluorescence spectra of the samples with a degree of substitution greater than 50% (6.4b - 6.4d) are superimposable in DMF and in THF (although the spectra are red-shifted in DMF compared to THF) indicating that the efficiency of inter-chromophore energy transfer is not affected by solvent in polymers with a relatively high degree of substitution.

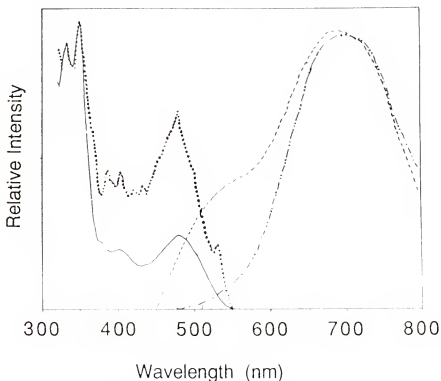


Figure 6.7. Fluorescence and fluorescence excitation spectra of PVP-CH=C(CN)₂ samples in DMF solution; {5a (40% functionalized), 5b (75%), 5c (88%), 5d (99%)}. (—) excitation of 5a ($\lambda_{em} = 700$ nm); (.....) excitation of 5c ($\lambda_{em} = 700$ nm); (---) fluorescence of 5a ($\lambda_{ex} = 350$ nm); (---) fluorescence of 5b and 5c ($\lambda_{ex} = 350$ nm), and 5a-5d ($\lambda_{em} = 460$ nm), all superimposed.

6.3 Experimental Section

6.3.1 General Preparations

PVP, PVP-CHO (5.5d) and PVP-CH=C(CN)₂ (6.4) were prepared as described in Chapter 5. The PVP has a $M_w = 15,200$ and a $M_w/M_n = 1.23$, and was used throughout this investigation as the starting material for further functionalization. 1-Nitropyrene, pyrene-1-carboxaldehyde and 1-aminopyrene, purchased from Aldrich, were purified by either repeated recrystallization from 95% ethanol or sublimation. Dicyanovinylpyrene was prepared from the condensation of pyrene-1-carboxaldehyde and malononitrile [90M1]. Photophysical measurements and instruments used in this investigation have also been described in Chapter 2.

6.3.2 Preparation of PVP-NO₂ (6.2)

A mixture of nitric acid (70%, 0.52g, 5.8 mmol) and acetic acid (10 ml) was added dropwise to PVP (2.0 g, 8.8 mmol of pyrene units) in chlorobenzene (50 ml) at 50-55°C. The clear dark-red solution was kept at this temperature for about 30 min., and then poured into acetone (200 ml) to precipitate the nitrated polymer. The remaining free acid was removed by extracting the polymer continuously with acetone in a Soxhlet. The golden-colored product (2.2 g) was obtained after being dried at 50°C under reduced pressure overnight.

6.3.3 Preparation of PVP-NH₂ (6.3)

To PVP-NO₂ (1.0 g, ~2 mmol -NO₂, 6.2) in THF (50 ml) SnCl₂·2H₂O (1.35 g, 6.0 mmol) in concentrated HCl (1.0 ml, 10 mmol) was added, and the mixture was refluxed for 3 - 4 hours. Addition of 95% ethanol (100 ml) precipitated the polymer which was further purified by repeated precipitation from its clear THF solution with 95% ethanol. The product (0.80 g) has a grey color after being dried as above.

6.3.4 Preparation of PVP-Br (5.1)

This preparation was adapted from that used for bromination of crosslinked poly(styrene) [76JOC3877]. PVP (4.0 g, 17.5 mmol) and Tl(OAc)₃ (0.13 g, 0.35 mmol, 2% of the pyrene units in mole) were dissolved in chlorobenzene (100 ml) and stirred for an hour at 25°C in the dark. Bromine (1.6 g, 10.0 mmol) in chlorobenzene (5 ml) was then added carefully to the solution at -78°C. The reaction mixture was warmed to 25°C and kept for another three hours. The precipitate (crosslinked polymer) was filtered and the brominated PVP was separated from the clear chlorobenzene solution by the addition of acetone (300 ml). The product (3.2 g) was obtained after being purified and dried as described for 6.2. The crosslinked PVP-Br weighted 1.2 g after being purified and dried.

6.4 Conclusions

The significance of the present study lies in the fact that the photophysical properties of the substituted PVPs can be tailored, either by functionalizing with a suitable substituent, or by varying the degree of substitution. As a result, fluorescent materials which emit at a variety of wavelengths can easily be prepared.

Energy transfer from the pyrene chromophore to the substituted pyrene chromophore in partially substituted samples clearly occurs. Remarkably, the degree of solvation of the polymer apparently influences the efficiency of energy transfer.

With the functionalization methods now developed, especially the formylation procedure, the chemical modification of linear PVP has become quite straightforward. Furthermore, formylation provides a route into a variety of functionalized PVPs. For example, the reaction of PVP-CHO with substituted phenylacetic acids ($R-C_6H_4-CH_2COOH$), which are available commercially, would result in a class of PVP-CH=CH- C_6H_4-R polymers with extended conjugation. The Schiff bases from PVP-CHO and 4-nitroaniline, or other nitroaminoaromatics, may also be readily prepared. Such functionalized polymers may have potentially useful photophysical or nonlinear optical properties.

CHAPTER 7
INTRAMOLECULAR CHARGE TRANSFER PROPERTIES OF $\text{ArCH}=\text{C}(\text{CN})_2$

7.1 Introduction

Compounds with aromatic or substituted aromatic donors and cyano or cyanovinyl acceptors have been the subject of many interesting investigations regarding both their intermolecular and intramolecular charge transfer (CT) properties. Intermolecular complex formation between condensed aromatics and tetracyanoethylene (TCNE) in solution [58JA2778] and in crystals [62JCP457] has been studied during the past 25 years. Recent studies have focused on intramolecular CT (ICT) interactions between aromatic donors and dicyanovinyl acceptors across rigid saturated spacers [87JA3285]. These ICT states are believed to be achieved through conformational folding which brings the donor and acceptor (D-A) into parallel planes at suitable through-space distances [65JCP3163, 76JA1095].

In the cases when the D-A is directly connected by a covalent single bond, the so called twisted intramolecular CT (TICT) state has been suggested [77CPL315]. A recent literature survey shows that many of these compounds still comprise aromatic donors with directly attached cyano groups [83PAC245].

We rationalized that the class of compounds of Figure 7.1 should exhibit excellent ICT properties since the aromatic donor groups are directly conjugated to a strong dicyanovinyl acceptor (The electron affinity of 2,2-dicyanoethylene was estimated to be 1.54 eV [76JA937]). The delocalization of the aromatic π electrons to an empty orbital of low energy in the acceptor could push the electron transfer and facilitate the electron transition process. Therefore, it should be possible to observe the ICT transitions in both directions (absorption and emission) in this investigation. The ICT absorptions are usually not observed in compounds where D-A groups are separated [87JA3285], nor for system of weak D-A even if they are directly connected [89JPC7092].

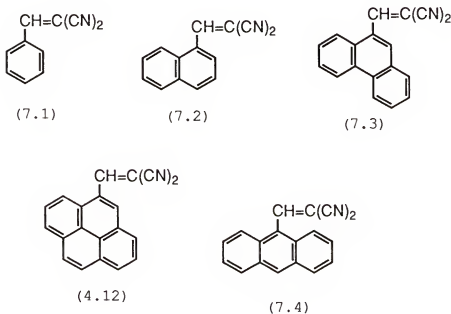


Figure 7.1. Structures of $\text{ArCH}=\text{C}(\text{CN})_2$

One of the important features of the present work is the study of the ground state properties of the compounds. The understanding about their electronic and geometric properties before the compounds are being excited has become one of the essential parts in the establishing of the mechanism of electron transfers.

7.2 Results and Discussion

7.2.1 Ground State Properties

Several interesting features emerge from study of the ^{13}C NMR spectra of compounds 7.1 to 7.4, 4.12. First, the resonance for the two vinyl carbons (denoted α and β to indicate their position relative to the aromatic ring, see Figure 7.2) are widely separated. For each of the

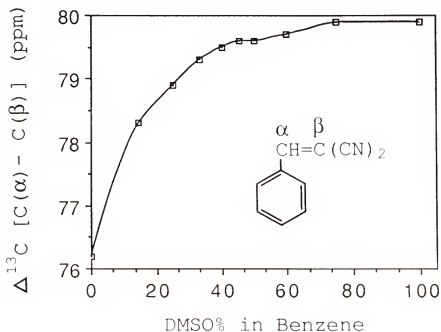


Figure 7.2. Plot of $\Delta^{13}\text{C}$ vs solvent polarity

Table 7.1
Ground State Properties of $\text{ArCH}=\text{C}(\text{CN})_2$

compound	mp(°C)	$\Delta^{13}\text{C}(\text{ppm})^a$	I.P.(eV) ^b	$\mu_g(\text{D})^c$	a(A) ^d	θ^e
$\text{PhCH}=\text{C}(\text{CN})_2$	85-86	79.9(161.5-81.6)	9.66(9.25)	4.87	3.6	5.3
$\text{NaphCH}=\text{C}(\text{CN})_2$	171-172	75.0(159.7-84.7)	9.08(8.12)	4.70	3.7	45.1
$\text{PhenCH}=\text{C}(\text{CN})_2$	203-205	75.2(161.3-86.1)	8.94(8.03)	5.27	4.4	2.2
$\text{PyreCH}=\text{C}(\text{CN})_2$	254-255	75.8(158.8-83.0)	8.48(7.41)	6.16	4.7	1.6
$\text{AnthCH}=\text{C}(\text{CN})_2$	210-212	70.6(162.4-91.8)	8.48(7.40)	4.36	4.0	70.5

^a The chemical shift differences $\{\text{C}(\alpha)-\text{C}(\beta)\}$ of the two vinyl carbon atoms, ^1H decoupled ^{13}C NMR taken at room temperature in DMSO. ^b The ionization potentials(I.P.) obtained from AM1 calculations. The values in parentheses are the I.P. of parent aromatics [80AM1199]. ^c Estimated from AM1 calculations. ^d Values estimated as 40% of the longest axis (calculated from AM1) of the corresponding compounds. ^e The dihedral angle between the aromatic ring and the plane of the dicyanovinyl substituent (from AM1 calculations).

compounds the resonances for the α and β carbons appear at 155 - 160 ppm and 80 - 90 ppm, respectively (Table 7.1). The significant difference in the chemical shift indicates that the two ethylenic carbon atoms experience a widely different electronic environment; the α carbon is deshielded while the β carbon is shielded. This observation implies that the ethylene group is highly polarized in the ground state. The second interesting feature is that the difference in the chemical shift for the α and β carbons ($\Delta^{13}\text{C}$) varies with solvent polarity. Figure 2 shows a plot of $\Delta^{13}\text{C}$ for 7.1 as a function of volume fraction of DMSO in benzene. As can be seen, $\Delta^{13}\text{C}$ increases sharply as the volume fraction of the polar solvent DMSO increase up to about 40%, where the $\Delta^{13}\text{C}$ is almost as great as in pure DMSO. Similar changes in $\Delta^{13}\text{C}$ were observed for the rest of the compounds in DMSO/benzene mixtures, as well as in other polar solvents. The increase in $\Delta^{13}\text{C}$ with increasing solvent polarity suggests that the ground state polarization of the ethylene group increases with solvent polarity.

The geometry and several ground state properties of 7.1 - 7.4, 4.12 were calculated by using the AM1 semiempirical method [85JA3902]. Table 7.1 contains a compilation of some of these results: (1) the calculated twist angle between the plane of the aromatic ring and the plane of the dicyanovinyl group (θ); (2) the calculated ground state dipole moment (μ_g); (3) the calculated first

ionization potential (IP); and (4) the radius of a spherical cavity in which the molecule fits (Onsager model [36JA1486], estimated as 40% of the long axis of the molecule). The validity of the computation is supported by the fact that the AM1 calculated bond lengths, bond angles, and dihedral angles of 7.1 are in excellent agreement with the experimental values which were determined from the crystal structure [69CRA1236]. Furthermore, the calculated IP values of the compounds correlate well with the IP values of the corresponding parent aromatic hydrocarbons (Table 7.1). As expected, in each case the IP's of the dicyanovinyl substituted compounds are slightly larger than those of the parent aromatics. The calculated dipole moment of the compound 7.1 (4.87 D), however, is somewhat lower than those reported (5.44 D [67CRA264] and 5.28 D [66TFS2084]). This deviation should not be significant, since relative values are utilized in the ensuing discussions.

A significant result of the computation is that in the AM1 optimized geometry the dihedral angle (θ) is small for compounds 7.1, 7.3, and 4.12 while for the naphthalene and anthracene substituted dicyanoethylene (7.2 and 7.4) the angle large. The calculation suggests that in the lowest energy conformer of 7.4 the plane containing the dicyanovinyl group is approximately 70° relative to the anthracene ring plane. The twist in 7.2 and 7.4 very likely results from unfavorable steric interactions between the neighboring aromatic hydrogens and the dicyanovinyl

group. The comparatively large dihedral angle in 7.2 and 7.4 should lead to a smaller ground state interaction between the D-A in these compounds as compared to 7.1, 7.3, and 4.12 where the two π orbital systems are nearly coplanar. This decreased interaction is reflected in the AM1 calculations by the fact that the ground state dipole moment (μ_g) of 7.4 (4.30 D) is smaller than the planar analog 7.3 (5.27 D) despite the fact that 7.4 has a smaller IP than 7.3.

7.2.2 Electronic Absorption Spectra

The electronic absorption spectra of compounds 7.1 - 7.4 in THF are shown in Figure 7.3A, and 4.12 in THF and cyclohexane in Figure 7.3B. An important feature of the UV spectra is the broad, long-wavelength absorption bands.

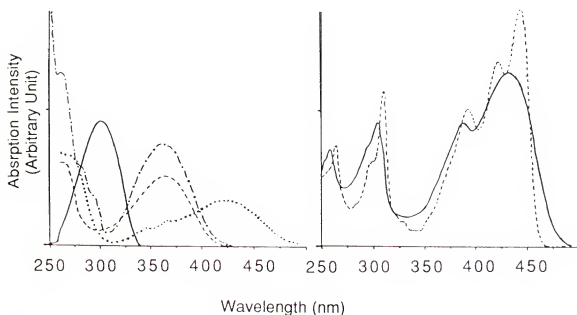


Figure 7.3. The absorption spectra of $\text{ArCH}=\text{C}(\text{CN})_2$. (A): (—) $\text{PhCH}=\text{C}(\text{CN})_2$, (---) $\text{NaphCH}=\text{C}(\text{CN})_2$, (-·-·-) $\text{PhenCH}=\text{C}(\text{CN})_2$, (····) $\text{AnthCH}=\text{C}(\text{CN})_2$ in THF; (B): (—) $\text{PyreCH}=\text{C}(\text{CN})_2$ in THF, (---) $\text{PyreCH}=\text{C}(\text{CN})_2$ in cyclohexane.

These bands can not be attributed to the transition to the locally excited (LE) state of the aromatic chromophore since the parent aromatics benzene, naphthalene, anthracene and phenanthrene do not absorb appreciably above 300 nm, and the lowest energy absorption of pyrene occurs at 334 nm. While in Figures 7.3 the dominant transition in THF for $\text{PhCH}=\text{C}(\text{CN})_2$ is at 307 nm ($\epsilon = 2.04 \times 10^4$), $\text{NaphCH}=\text{C}(\text{CN})_2$ at 367 nm ($\epsilon = 1.40 \times 10^4$), $\text{PhenCH}=\text{C}(\text{CN})_2$ at 369 ($\epsilon = 1.75 \times 10^4$), $\text{PyreCH}=\text{C}(\text{CN})_2$ at 442 ($\epsilon = 2.90 \times 10^4$) and 395 ($\epsilon = 2.06 \times 10^4$), and $\text{AnthCH}=\text{C}(\text{CN})_2$ at 430 ($\epsilon = 7.3 \times 10^3$). Furthermore, these new absorptions are characterized with a broad band shape which is common for CT transitions. Apparently, they are the ICT absorptions of the compounds. The LE absorptions, however, were still observed except for 7.1, although they are less pronounced than the ICT bands and blue-shifted relative to those of the parent aromatics. The linear correlation between the absorption frequencies of compound 7.1 - 7.4, 4.12 and the IP of the corresponding parent aromatics, or the IP of 7.1 - 7.4, 4.12 estimated from AM1 method, as shown in Figure 4, is another strong evidence for being ICT transitions. The use of the IP of the parent aromatics is validated by the fact that compound 7.1 - 7.4, 4.12 bear the same acceptor. The direct correlation between the IP's and CT absorption maxima has been documented for both intramolecular [80AMI199] and intermolecular [62JCP457] complexes.

Interestingly, Two ICT absorption bands were observed in the UV absorption spectra of 4.12 in all the polar

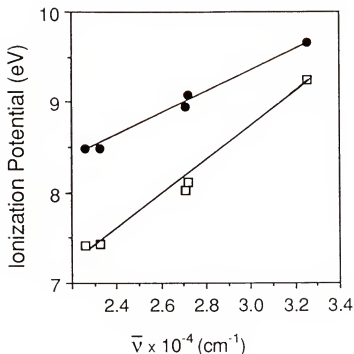


Figure 7.4. Plot of ICT absorption maxima vs ionization potentials of the compounds (●), and ionization potentials of the corresponding parent aromatics (◻).

solvents (Figure 7.3B). The second CT band was assigned to the transition from the molecular orbital immediately below the HOMO. The appearance of a second ICT band was previously noticed in the intermolecular complexes consisting of TCNE and condensed aromatic compounds both in the solid state and in solutions [62JCP457]. Of compound 7.1 - 7.4, 4.12, only the most heavily delocalized 4.12, which has the smallest energy gap between the HOMO and the next bonding orbital, shares such a transition in solution. The first ICT band of 4.12 shows additional splitting in nonpolar solvents such as cyclohexane (Figure 7.3B), probably due to the vibronic absorptions. This additional splitting was not observed in the rest of the compounds.

It is obvious that the molar extinction coefficients (ϵ) of the ICT absorption bands should reflect D-A interactions in the ground state. Such an interaction is at a maximum in the planar conformation as it was discussed earlier. Any twisting between donor and acceptor reduces the interaction and thus the intensity of the ICT absorptions. In the present case, ϵ is in the order of 4.12 > 7.1 > 7.3 > 7.2 > 7.4 (see Table 7.2), and is evidently related more to the twist angles in their ground states than to the donor abilities. The comparison of ϵ between compound 7.2 and 7.3, 7.4 and 4.12, respectively, are especially persuasive since the vertical ionization potential of naphthalene (8.12 eV) is very close to phenanthrene (8.03 eV), so does anthracene (7.40 eV) to

Table 7.2
Excited State Properties of Compounds $\text{ArCH}=\text{C}(\text{CN})_2$

compounds	UV Max. ₁ (nm) ($\xi \times 10^{-4}$) ^a	$\nu_n(0)$ (nm) ^b	$\mu_e(\text{D})$ ^c	$\mu_e - \mu_g(\text{D})$
PhCH=C(CN) ₂	307(2.04)	---	---	---
NaphCH=C(CN) ₂	367(1.40)	383	7.9	3.2
PhenCH=C(CN) ₂	369(1.75)	396	9.8	4.5
PyreCH=C(CN) ₂	442(2.90) 395(2.06)	420	10.9	4.7
AnthCH=C(CN) ₂	430(0.73)	470	7.0	2.6

^a Maxima of the C.T. absorption bands taken in THF at room temperature with a concentration of 5×10^{-5} M. ^b Derived from the intercept in Table 7.3. ^c Calculated from the slope in Table 7.3.

pyrene (7.41 eV), and both compounds 7.3 and 4.12 are planar. The twisting between D-A, therefore, appears to be the main reason for the low ϵ in 7.2 and 7.4.

The results from the UV absorption spectra suggest that the molecular orbital of the parent aromatics has been rearranged significantly since the introduction of the strong dicyanovinyl acceptor.

7.2.3 Fluorescence Studies

The emission properties of compound 7.1 - 7.4, 4.12 were studied in eight solvents of varying polarities. Fluorescence data, obtained by exciting at their respective ICT absorption frequencies of 7.2 - 7.4, 4.12, are summarized in Table 7.3. Compound 7.1 does not emit. The emission and excitation spectra of 4.12 is further presented in Figures 7.5 as a typical example. The quantum yields of 7.2 - 7.4, 4.12 were also measured. The values increase with increasing solvent polarity as can be seen from Table 7.3. However, they are small and could be barely detectable for 7.2 - 7.4.

In general, compound 7.2 - 7.4, 4.12 displays broad emissions which are highly solvent dependent, and are devoid of anything attributable to the donor chromophores. They were assigned to the ICT emissions. The assignment was based on mainly two facts: 1) the observed ICT absorptions of 7.1 - 7.4, 4.12 as have been discussed; 2) the characteristics of the emission spectra, broad, red-shifted and highly solvatochromic, which are similar to

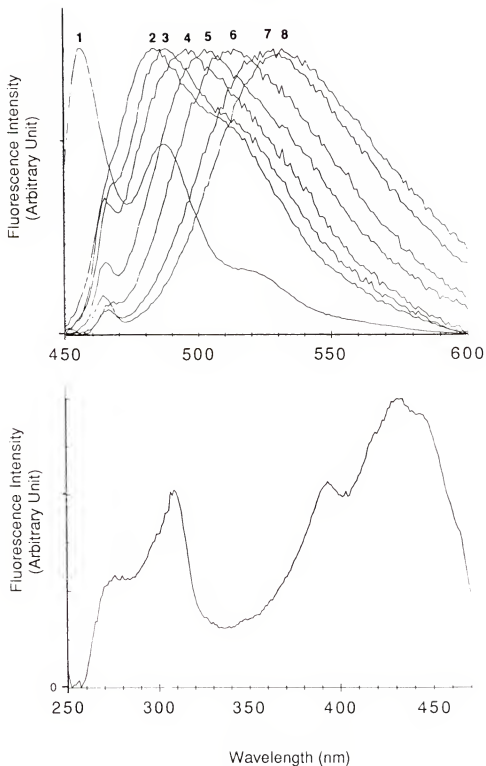


Figure 7.5. (A): Fluorescence spectra of PyreCH=C(CN)_2 ($\lambda_{\text{ex}} = 420 \text{ nm}$). Solvents: 1) cyclohexane, 2) toluene, 3) 1,4-dioxane, 4) ethyl acetate, 5) THF, 6) dichloromethane, 7) DMF, 8) acetonitrile; (B): Excitation spectrum of PyreCH=C(CN)_2 in THF ($\lambda_{\text{ex}} = 520 \text{ nm}$).

Table 7.3
Fluorescence Data of $\text{ArCH}=\text{C}(\text{CN})_2^a$

solvents	Δf	-----Ar-----		
		Naph	Phen	Anth Pyre
Toluene	0.126	2.288	2.247	2.020 2.049(0.003)
1,4-Dioxane	0.122	2.242	2.188	1.923 2.028(0.003)
Diethyl Ether	0.251	2.283	2.247	1.923 2.062(0.003)
Ethyl Acetate	0.292	2.222	2.200	1.904 2.000(0.003)
THF	0.308	2.237	2.202	1.901 1.988(0.004)
CH_2Cl_2	0.319	2.198	2.183	1.876 1.953(0.003)
DMF	0.377	2.119(0.001)	2.110(0.001)	1.834 1.894(0.005)
CH_3CN	0.393	2.008(0.001)	1.869(0.001)	1.818 1.887(0.004)
Intercept $\times 10^{-4}$ (cm^{-1}) ^b		2.611	2.525	2.127 2.381
Slope $\times 10^{-4}$ (cm^{-1})		1.27	1.14	0.76 1.17

^a Values are emission Max. $\times 10^{-4}$ cm^{-1} (quantum yield). The quantum yield is not listed if it is less than 0.001. ^b Both the slope and intercept were obtained from Figure 7.6 which do not include all the data listed.

those reported CT and ICT emissions [87JA3258, 90JA1214, 89JPC7092].

Comparison of Figure 7.5B and Figure 7.3B clearly indicates that the fluorescence excitation spectrum of 4.12 matches its UV absorption spectrum, which is also true for 7.2 - 7.4. The positions of the emission maxima listed in Table III are thus independent of the excitation energy.

Notably, although two ICT absorption bands were observed in the UV spectrum of 4.12, direct radiative decay to the orbital below the HOMO was not observed. Excitation at the second ICT absorption frequency of 4.12 produced an identical emission spectrum. The emission of 4.12, similar to its first ICT absorption band, displayed a structured fluorescence spectrum in nonpolar solvent cyclohexane. The origin of this splitting is still not clear.

The overall solvent effect on the position of CT fluorescence can be expressed as Eq. 7.1 [67JCP1183]. The equation has been used successfully in the literature to correlate solvent polarity with the solvatochromism of CT emissions [90JA1214, 87JA3258, 89JPC7092].

$$V_n = V_n(0) - 2\mu_e^2 \Delta f / hca^3 \quad \text{Equation 7.1}$$

$$\Delta f = [(\epsilon - 1)/(2\epsilon - 1)] - [(n^2 - 1)/(4n^2 + 2)]$$

The a values, which denotes the radius of the solvent cavity surrounding the molecule, have been included in Table 7.1. The fluorescence emission maxima of 7.2 - 7.4, 4.12 were thus tabulated against the solvent polarity

parameter (Δf) and shown in Figure 7.6. The slopes and intercepts of the curves in Figure 7.6 are listed in Table 7.3. The points which lie off the general trend on the left of the figure are those from toluene and 1,4-dioxane. The unusually low emission energies of the compounds in toluene suggests the possible presence of additional stabilization in the relaxation process of the excited state. This may result from the specific interactions between the aromatic π electron clouds of the solute and solvent. The dimension of this stabilization energy is about 2500 cm^{-1} (0.3 eV) at the present case. Similar

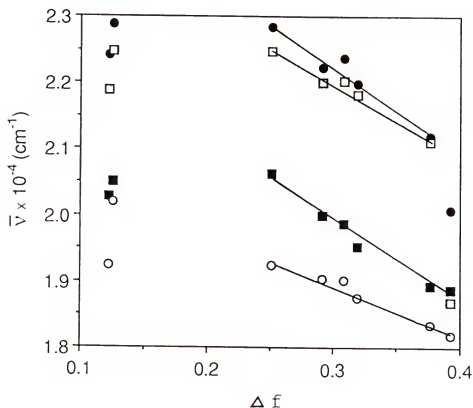


Figure 7.6. Fluorescence maxima as a function of solvent polarity parameter Δf , (●) NaphCH=C(CN)₂, (◻) PhenCH=C(CN)₂, (○) AnthCH=C(CN)₂, (■) PyreCH=C(CN)₂.

effect has been reported when benzene was used as the solvent for compounds containing aromatic donors [87JA3258]. The deviation in 1,4-dioxane is expected. It is commented in a recent review [90JPP293] that 1,4-dioxane is a 'pseudo-polar' solvent with solvatochromic effects similar to that of cyclic ethers like THF. Literature survey shows that this solvent has hardly been included in published linear correlations between Δf and the positions of emission [90JA1214, 87JA3258, 89JPC7092]. The Δf value of this solvent can be better established by considering its chair conformation.

The slope ($2\mu_e^2/hca^3$) in Figure 7.6 reflects the solvatochromic sensitivity of compound 7.2 - 7.4, 4.12. Apparently, the behavior of the compounds in the excited states is quite different as evidenced by their slopes, which differ from 7.6×10^3 to 1.27×10^4 cm^{-1} . The excited state dipole moments (μ_e), calculated by Equation 1 from the slopes listed in Table 7.3, ranges from 7 to 11 D (Table 7.2). These values appear to be lower than those of isolated D-A compounds (> 20 D) [90JA1214], or TICT forming compounds (> 15 D) [89JPC7092], possibly due to the small molecular dimensions. Interestingly, the estimated μ_e 's are related to the twist degree calculated from AM1 (Table 7.1). The more the twisting between the donor and acceptor planes in the ground state is, the less the values are.

7.2.4 Solvatochromic Shifts of ICT Absorption Bands

It is believed that polar solvents induce red-shift of ICT absorptions, although it is less distinct than in the emission spectra. The first absorption band of some ICT forming compounds such as 2-methoxyacetophenone, 4-nitroanisole and fluoroaniline were previously reported to undergo red-shift as solvent polarity increases, provided that the solvents have the same refractive indices [90JPP293, 87SP1317]. Tseng and Singer [89JCP7092] in their study of ICT-forming compounds even stated: 'there are little or no CT contributions to the absorption spectra as indicated by only very modest red shifts in going from cyclohexane to acetonitrile as solvent'. However, in another very recent paper, Hermant et al. studied highly fluorescent rod-shaped intramolecular donor-acceptor systems and pointed out that their absorption spectra displayed negligible solvatochromism [90JA1214].

In order to clarify some of the existing ambiguities, the ICT absorption maxima of 7.1 - 7.4, 4.12 were measured in a series of solvents ranging from 1,4-dioxane and toluene to DMF and acetonitrile (Table 7.4). Figure 7.7A tabulated these ICT absorption maxima of compound 7.1 - 7.4 as the function of the solvent polarity parameter Δf , and Figure 7.7B the first three absorptions of compound 4.12.

Similar to the emission spectra in Figure 7.6, toluene possesses the strongest solvation ability among the solvents tried, although it is one of the least polarsolvents. The first ICT absorption bands of all the

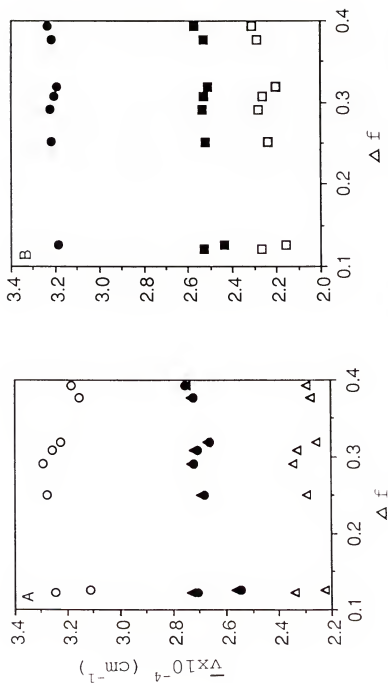


Figure 7.7. Plot of ICT absorption maxima vs solvent polarity parameter Δf . (A): (○) PhCH=C(CN)₂, (▲) NaphCH=C(CN)₂, (●) PhCH=C(CN)₂, (Δ) AnthCH=C(CN)₂, (B): The first three absorption maxima of PyreCH=C(CN)₂.

Table 7.4
Intramolecular Charge Transfer Absorption Maxima of
ArCH=C(CN)₂^a

solvent	-----Ar-----					
	Ph	Naph	Phen	Anth	Pyre(1)	Pyre(2) ^b
Toluene	3.115	2.564	2.545	2.227	2.160	2.439
Diethyl Ether	3.279	2.695	2.681	2.294	2.237	2.525
1,4-Dioxane	3.247	2.732	2.710	2.336	2.268	2.532
THF	3.257	2.725	2.710	2.326	2.262	2.532
Ethyl Acetate	3.290	2.732	2.725	2.342	2.278	2.538
CH ₂ Cl ₂	3.226	2.674	2.660	2.257	2.203	2.513
DMF	3.155	2.732	2.725	2.278	2.288	2.532
CH ₃ CN	3.185	2.747	2.755	2.294	2.310	2.571

^a Values are UV Max. $\times 10^{-4}$ cm⁻¹. ^b The second charge transfer bands of compound 4.12.

compounds are more red shifted in toluene than in any other solvent examined including DMF and acetonitrile. This may reflect specific interactions between the aromatic electrons of the solute and solvent, as it has been discussed earlier. Besides in toluene, the magnitude of fluctuation is almost negligible (< 2000 cm⁻¹), and there is not a systematic variation in ν as the function of polarity in Figure 7.7A. The transitions from orbitals of energy below HOMO are even less affected by the solvent environment as is shown in Figure 7.7B. The third transition of 7.4, assigned to a local excitation of the donor, is of almost constant wavelengths in all the solvents.

on the other hand, the solute-solvent interaction is very similar among compound 7.2 to 7.4, 4.12, as demonstrated by the good linear correlations when the first ICT absorption maxima of 7.2 were plotted against the others (Figure 7.8).

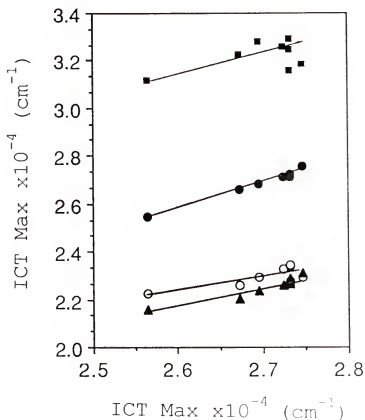


Figure 7.8. Plot of the absorption maxima of NaphCH=C(CN) $_2$ in various solvents vs that of (■) PhCH=C(CN) $_2$, (●) PhenCH=C(CN) $_2$, (▲) AnthCH=C(CN) $_2$ and (○) PyreCH=C(CN) $_2$ in the same solvent.

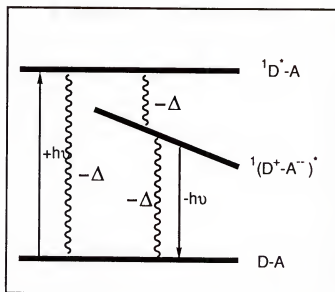
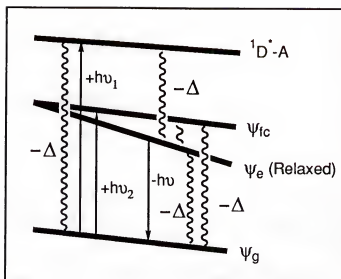
The above results have clearly indicated that solvent polarity has no systematic effect on the energy of ICT absorptions. The perturbation of the solution, or solvent effects, may result in either red or blue shift for

the ICT absorptions, depending on the pattern of solute-solvent interaction. The theoretical background of this argument will be furnished in the following section. Some published equations, such as the ratio method for the estimation of excited state dipolar moment [83CPL272] (Eq. 2), should thus be used with caution.

$\mu_e = \mu_g \{ \Delta E_{flu} / \Delta E_{abs} \}$ (if μ_g and μ_e are colinear) Equation 7.2

7.2.5 The ICT Mechanism

The observations of strong ICT absorptions lying at a lower energy level than those of the parent aromatic donor absorptions; of the perfect matching between the UV spectra and the fluorescence excitation spectra, of the strong solvatochromic effect of the emission spectra, and of the only ICT emissions irrespective of the excitation energy, have supported a Jablonski diagram depicted in Figure 9A. Where the ψ_g denotes the ground state, ψ_e the solvent relaxed ICT excited state, ψ_{fc} the Franck-Conton excited state, and ${}^1D^*-A$ the locally excited donor energy level. The mechanism of the electron transfer regarding those ICT forming compounds with strong interaction between D-A in the ground state can thus be outlined as follows. The electron in the ICT forming compounds can be either excited to the ${}^1D^*-A$ or to the ψ_{fc} , depends on the external energy level. However, it undergoes a relaxation process to the solvent relaxed ψ_e state, regardless which excited state it was, prior to the radiative decay from ψ_e to ψ_g .





 Solvent Polarity

Figure 7.9. Simplified energy level diagram of intramolecular charge transfer forming compounds. (A): Type with strong interaction in the ground state; (B): Type without strong interaction in the ground state.

An supporting evidence of the mechanism comes from the $V_n(0)$ values, which are the intercepts of the solvatochromic emission curves in Figure 7.6. $V_n(0)$ is defined as the energy of gas-phase ICT emission maxima [90JA1214], and is thus the Franck-Condon excited state (ψ_{fC}). The ψ_{fC} , moreover, is coincident to the ICT absorption energy as is illustrated in Figure 7.8A. Therefore, $V_n(0)$ should be close to the ICT absorption position if the mechanism is reasonable. As can be seen from Table 7.2, the comparison of the two values (column 1 and 2) are quite satisfactory.

Figure 7.9B, reproduced for comparison, is a reported energy level diagram [85JA5839] for ICT forming compounds with weak interaction between D-A in the ground state. The differences between Figure 7.9A and 7.9B are significant and are further discussed by considering the wave functions. The wave function for the ground and excited states of a D-A complex, according to Mulliken's theory [52JA811], can be described by Eq. 7.3 and 7.4, respectively.

$$\psi_g = \underline{a}\psi(D-A) + \underline{b}\psi(D^+-A^-) \quad \text{Equation 7.3}$$

$$\psi_e = \underline{a}^*\psi(D^+-A^-) + \underline{b}^*\psi(D-A) \quad \text{Equation 7.4}$$

Where ψ_g is the ground state wave function, ψ_e the excited state, $\psi(D-A)$ the component of D-A without charge separation, and $\psi(D^+-A^-)$ the charge separated component. The \underline{a} and \underline{b} are the normalization coefficients for ψ_g , and

\underline{a}^* and \underline{b}^* for ψ_e . For a weakly interacted complex, $\underline{b} = \underline{b}^* = 0$, Equation 7.3 and 7.4 can be simplified to:

$$\psi_N = \underline{a}\psi(D-A) \quad \text{Equation 7.5}$$

$$\psi_E = \underline{a}^*\psi(D^+-A^-) \quad \text{Equation 7.6}$$

The solvent effect on the ground state can thus be neglected, as is shown in Figure 9B. Whereas for compound 7.1 - 7.4, 4.12, charge separation in the ground state has been clearly indicated by ^{13}C NMR (Figure 7.2). Equation 7.3 can therefore not be simplified, and ψ_g declines with increasing solvent polarity as is shown in Figure 7.9A. Another difference is about the ICT absorptions. There is not such an absorption energy level in Figure 7.9B and the emission spectra could only be obtained by exciting at the donor chromophores energy level. This is true for a weak D-A complex since there is almost no interaction present between the D-A in the ground state. Whereas in the present case, intense ICT absorption bands were observed in each of the compounds due to the presence of a strong D-A interaction in the ground state. Obviously, a energy level is present for the ICT state which lies below the $^1\text{D}^+-\text{A}$ and is parallel to ψ_g .

The established mechanism, in turn, has theoretically supported some of the arguments which have been proposed earlier. For example, the one about the independence of ICT absorption maxima on solvent polarity. Examination of Figures 9A and 9B indicates that ICT absorptions need not

necessarily to be solvatochromic. Since the Franck-Condon first excited state possesses a solvent configuration similar to that of the ground state, the energy differences between ψ_{fc} and ψ_g in Figure 7.9A, and between D-A and $1D^*-A$ in 7.9B is constant over the solvent polarity provided no specific interactions exists. Furthermore, the magnitudes of solvent dependences of absorptions are much smaller compared with those of the emissions, which are solvated to the ψ_e before the radiative decay.

7.3 Experimental Section

The 2,2-dicyanovinylaromatics shown in Figure 7.1 were prepared by condensing the corresponding aromatic aldehydes with malononitrile using piperidine as catalyst[80AMI199]. The compounds were purified by repeated recrystallization and sublimation. The high purity of the compounds is indicated by elemental analysis (within 0.20% of theory), clean 1H and ^{13}C NMR spectra and sharp melting points (see Table 7.1). The rest of the experimental details have been described in the Experimental Section of Chapter 2.

7.4 Conclusions

Values reflecting ground state properties such as ionization potential, dipole moment and geometry of the $ArCH=C(CN)_2$ were estimated by AM1 calculations, and found

to be in very good agreement with the limited data available in the literature. The geometry in the ground state, especially the degree of twisting between the donor and acceptor in these ICT forming compounds, appears to have a profound influence on their photophysical behaviors. For instance, the molar extinction coefficient, the dipole moment of both excited and ground state, and even the $\Delta^{13}\text{C}$ of the two vinyl carbon atoms decrease with increasing degree of twisting.

In contrary to the common believe, results suggest that the ICT absorption frequency is independent of the solvent polarity. At least, there are some stronger specific perturbations in the solution other than the function of solvent polarity in some cases. Therefore, there may not be a linear relationship between the absorption energy and solvent polarity present in solution. This argument is theoretically supported by the electron transfer mechanism proposed for ICT forming compounds with strong interaction between donor and acceptor in the ground state, and a similar mechanism in the literature [85JA5839] for ICT forming compounds with no strong interaction in the ground state.

BIBLIOGRAPHY

The reference system adopted in this dissertation is based on that used by Katritzky and Rees in "Comprehensive Heterocyclic Chemistry," Pergamon Press, New York, 1984, Vol. 4, p. 1085. Journal references are designated by a number-letter code, the first two digits of which denote the year of publication, the next one or more letters, the journal, and the final digits, the page number. Books, proceedings, and encyclopedia references are coded 'MI' (miscellaneous) and are listed according to the year of publication. If reference is made to an entire book, the textual designation includes only the year and the code (for example, [86MI]). Otherwise, the page number is included in the text (for example, [86MI110]). Patents are listed by year and are followed by the patent number (for example, [79USP4158093]).

<u>Code</u>	<u>Full Title</u>
AC(R)	<u>Ann. Chim. (Rome)</u>
ACS	<u>Acta Chem. Scand</u>
AMI	<u>Adv. Mol. Interact. Proce.</u>
B	<u>Biochem.</u>
BCJ	<u>Bull. Chem. Soc. Jpn.</u>
BPJ	<u>The British Polym. J.</u>

BSB	<u>Bull. Soc. Chim. Belg.</u>
CI(L)	<u>Chem. Ind. (London)</u>
CL	<u>Chem. Lett.</u>
CPL	<u>Chem. Phys. Lett.</u>
CRA	<u>C. R. Acad Sci., Paris</u>
GO	<u>Ger. Offen</u>
IEC	<u>Ind. Eng. Chem.</u>
JA	<u>J. Am. Chem. Soc.</u>
JCP	<u>J. Chem. Phys.</u>
JCS(P1)	<u>J. Chem. Soc., Perkin Trans. 1</u>
JCS(C)	<u>J. Chem. Soc., Chem. Commun.</u>
JHC	<u>J. Heterocycl. Chem.</u>
JKTK	<u>Jpn. Kokai Tokkyo Koho</u>
JMS(C)	<u>J. Macromol. Sci.-Chem.</u>
JOC	<u>J. Org. Chem.</u>
JOM	<u>J. Organomet. Chem.</u>
JPC	<u>J. Phy. Chem.</u>
JPP(A)	<u>J. Photochem. Photobio., A</u>
JPS	<u>J. Polym. Sci.</u>
JPS(A)	<u>J. Polym. Sci. Part A-1</u>
JPS(C)	<u>J. Polym. Sci.: Polym. Chem. Ed.</u>
JPS(L)	<u>J. Polym. Sci.: Polym. Lett.</u>
MA	<u>Macromolecules</u>
MC	<u>Makromol. Chem.</u>
MC(C)	<u>Makromol. Chem., Rapid Commun.</u>
MI	<u>Miscellaneous (Book or Encyclopedia)</u>
N	<u>Nature</u>
PAC	<u>Pure & Appl. Chem.</u>

PP	<u>Polym. Prep.</u>
RTC	<u>Recl. Trav. Chim. Pays-Bas</u>
S	<u>Science</u>
SA	<u>Spectrochim. Acta</u>
T	<u>Tetrahedron</u>
TFS	<u>Trans. Faraday Soc.</u>
TL	<u>Tetrahedron Lett.</u>
ZPC	<u>Z. Phys. Chem., N.F.</u>
ZE	<u>Z. Electrochem.</u>
37AC(R)1	H. Vollmann, H. Becker, M. Corell, H. Streeck, G. Langbein, <u>Ann.</u> , 1937, <u>531</u> , 1
38JA2555	L. F. Fieser, J. L. Hartwell, <u>J. Am. Chem. Soc.</u> , 1938, <u>60</u> , 2555
50JA1051	P. D. Bartlett, H. Kwart, <u>J. Am. Chem. Soc.</u> , 1950 <u>72</u> , 1051. And the references therein
51JA818	C. C. Price, B. D. Halpern, <u>J. Am. Chem. Soc.</u> , 1951, <u>73</u> , 818
51JA895	G. B. Butler, F. L. Ingley, <u>J. Am. Chem. Soc.</u> , 1951, <u>73</u> , 895
52JA811	R. S. Mulliken, <u>J. Am. Chem. Soc.</u> , 1952, <u>74</u> , 811
54ZPC275	T. Forster, K. Kasper, <u>Z. Phys. Chem., N. F.</u> , 1954, <u>1</u> , 275
57ZE961	E. Lippert, <u>Z. Electrochem.</u> , 1957, <u>61</u> , 962
58JA2778	R. E. Merrifield, W. D. Phillips, <u>J. Am. Chem. Soc.</u> , 1958, <u>80</u> , 2778
59JOC627	A. E. Miller, J. W. Biss, L. H. Schwartzman, <u>J. Org. Chem.</u> , 1959, <u>24</u> , 627
60JPS49	D. L. Lyman, <u>J. Polym. Sci.</u> , 1960, <u>45</u> , 49
60N1045	B. Stevens, E. Hutton, <u>Nature</u> , 1960, <u>186</u> , 1045

- 62JCP457 H. Kuroda, M. Kobayashi, M. Kinoshita, S. Takemoto, J. Chem. Phys., 1962, 36, 457
- 63JPS(A)1635 D. Katz, J. Polym. Sci., Part A, 1963, 1, 1635
- 64MI645 G. Goldfinger, Encyclopedia of Polymer Science and Technology, N. M. Bikales, H. F. Mark, N. G. Garlord (ed), Wiley & Sons, New York, 1964, p 645
- 65JCP3163 F. Hirayama, J. Chem. Phys., 1965, 42, 3163
- 65MI1 P. W. Morgan, Condensation Polymers: by Interfacial and Solution Methods, Interscience Publishers, New York, 1965, p 1
- 66EPJ219 T. Berezhnykh-Foldes, F. Tudos, European Polymer J., 1966, 2, 219
- 66TFS2084 H. Weiler-Feilchenfeld, I. Agranat, E. D. Bergmann, Trans. Faraday Soc., 1966, 62, 2084
- 67JCP1183 H. Beens, H. Knibbe, J. Chem. Phys., 1967, 47, 1183
- 67JOM(10)518 H. Hashimoto, M. Hida, S. Miyano, J. Organomet. Chem., 1967, 10, 518
- 67T985 E. Clar, B. A. McAndrew, M. Zander, Tetrahedron, 1967, 23, 985
- 68BCJ2719 K. Tanikawa, T. Ishizuka, K. Suzuki, S. Kusabayashi, H. Mikawa, Bull. Chem. Soc. Jpn., 1968, 41, 2719
- 68CPL535 B. Stevens, M. F. Thomaz, Chem. Phy. Lett., 1968, 1, 535
- 68JPS(L)275 K. Tanikawa, S. Kusabayashi, H. Hirata, H. Mikawa, J. Polym. Sci., Polym. Lett., 1968, 6, 275
- 69B4728 L. M. Dowling, G. R. Stark, Biochem., 1969, 8, 4728
- 69BCJ2406 K. Tanakawa, H. Hirata, S. Kusabayashi, H. Mikawa, Bull. Chem. Soc. Jpn., 1969, 42(8), 2406
- 69CRA1236 M. P. Auvray, M. J. Wyart, C. R. Acad. Sc. Paris, 1969, t.268, 1236

- 70JOC2707 M. D. Bentley, M. J. S. Dewar, J. Org. Chem., 1970, 35, 2707
- 70MI69 J. Odian (Ed.) Principles of Polymerization, McGraw-Hill, New York, 1970, p 69.
- 72CL499 M. Yokoyama, T. Tamamura, T. Nakano, H. Mikawa, Chem. Lett., 1972, 499
- 72JOC88 A. McKillop, D. Bromley, E. C. Taylor, J. Org. Chem., 1972, 37, 88
- 72JCP1746 J. R. McDonald, W. E. Echols, T. R. Price, R. B. Fox, J. Chem. Phys., 1972, 57, 1746
- 72JPS(A)1345 H. Kamogawa, J. Polym. Sci.: Part A-1, 1972, 10, 1345
- 72MA158 J. J. O'Malley, J. F. Yanus, J. M. Pearson, Macromolecules, 1972, 5, 158
- 72MI23 J. B. Birks, Organic Molecular Photophysics, Vol. 1, J. B. Birks, Ed., Wiley-Interscience, New York, 1973, P 23
- 73BCJ358 S. Yoshimoto, K. Okamoto, H. Hirata, S. Kusabayashi, H. Mikawa, Bull. Chem. Soc. Jpn., 1973, 46, 358
- 74JPS(C)247 D. C. Evans, M. H. George, J. A. Barrie, J. Polym. Sci. Polym. Chem., 1974, 12, 247
- 74JPS(C)2449 H. Kamogawa, J. Polym. Sci., Polym. Chem., 1974, 12, 2449
- 75JCS(C)225 J. M. J. Frechet, G. Pelle, J. Chem. Soc., Chem. Commun., 1975, 225
- 75JMS(C)97 D. H. Solomon, J. Macromol. Sci. -Chem., 1975, A9, 97
- 76JA937 K. N. Houk, L. L. Munchausen, J. Am. Chem. Soc., 1976, 98, 937
- 76JA1095 T. Mimura, M. Itoh, J. Am. Chem. Soc., 1976, 98, 1095
- 76JMS(C)923 D. G. Hawthorne, D. H. Solomon, J. Macromol. Sci.-Chem., 1976, A10, 923
- 76JOC3877 M. J. Farrall, J. M. J. Frechet, J. Org. Chem., 1976, 41, 3877

- 77CPL315 A. Siemiarczuk, Z. R. Grabowski, A. Krowczynski, M. Asher, M. Ottolenghi, Chem. Phys. Lett., 1977, 51, 315
- 78MI375 B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. D. Smith, A. R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, 4th. Ed, Longman, London, 1978, p.375
- 79PP165 R. Asami, H. Watanabe, N. Nakayama, Polym. Prep., 1979, 20, 165
- 80AMI199 J. -I. Aihara, K. Araya, K. Chiba, Y. Matsunaga, Adv. Mol. Relax. Interact. Proce., 1980, 18, 199
- 80BPJ55 D. A. Buckley, L. A. Teuscher, The British Polym. J., 1980, 55
- 80MI199 J. I. Aihara, K. Araya, K. Chiba, Y. Matsunaga, Advances in Molecular Relaxation Processes, 1980, 18, 199
- 82JPS(C)467 Y. Itoh, Y. Morishima, S-I. Nozakura, J. Polym. Sci., Polym. Chem. Ed., 1982, 20, 467
- 82JPS(C)2007 Y. Morishima, Y. Itoh, T. Hashimoto, S. -I. Nozakura, J. Polym. Sci., Polym. Chem. Ed., 1982, 20, 2007
- 83CPL272 P. Suppan, Chem. Phys. Lett., 1983, 94, 272
- 83MA1390 P. Collart, K. Demeyer, S. Toppet, F. C. De Schryver, Macromolecules, 1983, 16, 1390
- 83MI D. J. Williams (ed), Nonlinear Optical Properties of Organic and Polymeric Materials, ACS Symposium, Series 233, ACS, Washington D.C., 1983
- 83PAC245 Z. R. Grabowski, J. Dobkowski, Pure & Appl. Chem., 1983, 55, 245
- 84MI Y. R. Shen, The Principles of Nonlinear Optics, Wiley & Sons, New York, 1984
- 85JA3902 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, J. Am. Chem. Soc., 1985, 107, 3902
- 85JA5839 P. Pasman, G. F. Mes, N. W. Koper, J. W. Verhoeven, J. Am. Chem. Soc., 1985, 107, 5839

- 85JPS(C)585 A. Tsuchida, M. Yamamoto, Y. Nishijima, J. Polym. Sci., Polym. Chem. Ed., 1985, 23, 585
- 85MA882 S. Egusa, M. Sisido and Y. Imanishi, Macromolecules, 1985, 18, 882
- 85MA1026 P. Collart, S. Toppert, Q. F. Zhou, N. Boens, F. C. De Schryver, Macromolecules, 1985, 18, 1026
- 85MA1366 P. V. Kamat, R. Basheer, M. A. Fox, Macromolecules, 1985, 18, 1388
- 86MA2390 R. V. Todesco, R. A. Basheer, P. V. Kamat, Macromolecules, 1986, 19, 2390
- 86MC(C)549 K. Kondo, K. Takemoto, Makromol. Cehm., Rapid Commun., 1986, 7, 549
- 86MI489 J. R. Ellis, Handbook of Conducting Polymers, T. A. Skotheim (ed), Marcel Dekker, Inc., New York and Basel, 1986, p.489
- 87BCJ83 A. Itaya, K.-i. Okamoto, Bull. Chem. Soc. Jpn., 1987, 60, 83
- 87JA3258 H. Oevering, M. N. Paddon-Row, M. Heppener, A. M. Oliver, E. Cotsaris, J. W. Verhoeven, N. S. Hush, J. Am. Chem. Soc., 1987, 109, 3258
- 87JCS(P1)791 A. R. Katritzky, S. Rachwal, B. Rachwal, J. Chem. Soc., Perkin Trans. 1, 1987, 791
- 87JCS(P1)2673 A. R. Katritzky, K. Yannakopoulou, W. Kuzmierkiewicz, J. M. Aurecochea, G. J. Palenik, A. E. Koziol, M. Szczesniak, J. Chem. Soc., Perkin Trans. 1, 1987, 2673
- 87MI P. N. Prasad and D. R. Ulrich (ed), Nonlinear Optical and Electroactive Polymers, Plenum Press, New York, 1987
- 87RTC120 A. M. van den Braken-van Leersum, C. Tintel, M. van't Zelfde, J. Cornelisse, J. Lugtenburg, Recl. Trav. Chim. Pays-Bas, 1987, 106, 120
- 87SA1317 D. Noukakis, P. Suppan, Spectrochim. Acta, 1987, 43A, 1317

- 88MI A. J. Heeger, J. Orenstein, D. R. Ulrich (ed), Nonlinear Optical Properties of Polymers, Materials Research Society Symposium Proceedings, 109, Publishers Choice Book Mfg. Co., Mars, Pennsylvania, 1988
- 89JPS7092 J. C. C. Tseng, L. A. Singer, J. Phys. Chem., 1989, 93, 7092
- 89MA3495 A. R. Katritzky and D. W. Zhu, Macromolecules, 1989, 22, 3495
- 89MI J. Messier, F. Kajazar, P. Parasad, D. R. Ulrich (ed), Nonlinear Optical Effects in Organic Polymers, NATO ASI Series, Kluwer Academic Publishers, Dordrecht, Boston and London, 1989
- 90JA1214 R. M. Hermant, N. A. C. Bakker, T. Scherer, B. Krijnen, J. W. Verhoeven, J. Am. Chem. Soc., 1990, 112, 1214
- 90JPC2740 K. S. Schanze, L. A. Cabana, J. Phys. Chem. 1990, 94, 2740
- 90JPP293 P. Suppan, J. Photochem. Photobio., A: Chem. 1990, 50, 293
- 90MA A. R. Katritzky, D. -W. Zhu, Macromolecules, in press.
- 90MI1 A. R. Katritzky, D. -W. Zhu, K. S. Schanze, J. Phy. Chem., submitted for publication

BIOGRAPHICAL SKETCH

Dong-Wei Zhu was born on August 21, 1960, in Zhejiang, Mainland China. He was raised in the so called "Cultural Revolution" period (1967-1977) in China, one of the darkest intervals in over two thousand years of Chinese history, when nobody studied in school and no teacher could do his job. His real education started in 1978 when that period ended and he became part of the first group of college students in more than a decade. After four years of intensive study, Hangzhou University awarded him an B.S. degree in chemistry in early 1982, Three years later, he received an M.S. degree in polymer chemistry from the same University.

His further education was continued in North America. After one year of graduate study at the University of British Columbia, he joined Dr. Katritzky's group here at the University of Florida in August, 1987, to work toward his Ph.D. degree.

He got married in 1986 in Mainland China and had a son in 1988 in the United States. However, He has not had a chance to see his parents for four years.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Alan R. Katritzky
Kenan Professor of Chemistry

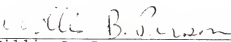
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Kirk S. Schanze
Assistant Professor of Chemistry

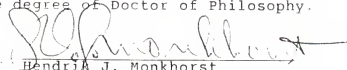
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Jonathan E. Enholm
Assistant Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Willis B. Person
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Hendrik J. Monkhorst
Professor of Physics

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1990

Dean, Graduate School